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"Synthesis and Characterization of Dipolar Organic Molecules for Nonlinear Optical Materials"

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"Synthesis and Characterization of Dipolar Organic Molecules for Nonlinear Optical Materials"

A Trident Scholar Project Report

by

Midshipman Dennis J. Rivet II, Class of 1992

U.S. Naval Academy

Annapolis, Maryland

William T. Lavell

Adviser: Assistant Professor William T. Lavell
Chemistry Department

Accepted for Trident Scholar Committee

Francis D Correll

Chair

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The object of this investigation is to design, synthesize, and characterize novel organic materials for efficient second-harmonic generation. Secon-harmonic generation is a nonlinear optical phenomenon that can be observed for a variety of inorganic and organic materials, some of which have been incorporated into electrical devices to perform various operations. While most devices at the present time utilize inorganic compounds, the search for highly efficient and easily processable materials has led tc the investigation of various classes of organic compounds.
In this project, the synthesis of three general classes of molecules was attempted: (a) amphiphilix azo dyes, (b) polymeric p-(dialkyamino)arylamines, and (c)poly(pyridine vinylene). These molecules appear to possess the electronic and structural properties necessary for efficient second-harmonic generation.

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ABSTRACT

The object of this investigation is to design, synthesize, and characterize novel organic materials for efficient second-harmonic generation. Second-harmonic generation is a nonlinear optical phenomenon that can be observed for a variety of inorganic and organic materials, some of which have been incorporated into electrical devices to perform various operations. While most devices at the present time utilize inorganic compounds, the search for highly efficient and easily processable materials has led to the investigation of various classes of organic compounds.

Efficient second harmonic generation by organic molecules is dependent upon two distinct material properties. First, the molecules must have a large molecular hyperpolarizability; typically, this is large for highly conjugated, dipolar organic molecules. Second, the molecules must be capable of being oriented in a noncentrosymmetric arrangement; typically, this can be accomplished by electric field poling, Langmuir-Blodgett techniques, self-assembly or interfacial partitioning. An alternative technique, that of orienting the chromophore within a diblock copolymer, was pursued.

In this project, the synthesis of three general classes of molecules was attempted: (a) amphiphilic azo dyes, (b) polymeric p-(dialkylamino)arylamines, and (c) poly(pyridinevinylene). These molecules appear to possess the electronic and structural properties necessary for efficient second-harmonic generation

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1.1 General Introduction to Materials

The stage of development of the human race is often measured by the materials of the age in which they exist. Early man depended upon his environment, and the materials that it provided, for his basic human needs: food, clothing and shelter. Trees provided lumber for building; soil and water combined to make mud; plants provided fibers that could be woven, as well as leaves, seeds and fruits that could be eaten. Caves provided dwelling places that were protected from the wind and the rain, and provided some control over the temperature.

Technological advances in tools, and the materials from which tools were made, allowed civilization to progress. We now categorize entire periods of time by their materials: stone, bronze and iron provided materials for tools, which in turn allowed for better agriculture, better hunting and better building. In time, steel was developed. Today, modern alloys provide high strength, low weight, inexpensive, corrosion-resistant materials, that are vitally important to the world's economy.

The discussion so far has been concerned primarily with structural building materials. In fact, building materials are only one class of materials that are important today. Also important are pharmaceutical materials, electrical materials and optical materials. The design and synthesis of novel materials for future applications are a significant part of the current research and development arena.

1.2 General Classes of Molecules

Organic molecules can be classified on the basis of size, shape, or charge distribution. Sizes of molecules can be broken down into small (50-500 amu), for example, methanol, gasoline, and amino acids; medium (500-1000 amu), such as smaller biomolecules and motor oils; and large (weight >1000 amu), which would include the polymeric materials our research focuses on. Shapes can range from linear, to spherical, to two or three-dimensional depending on the complexity of the molecule. The nature of the charge distribution is the most important parameter to consider. Molecules with a symmetrical arrangement of electrons are nonpolar, while unsymmetrical molecules are polar. These systems have regions of higher electron density and regions of lower electron density which give it a positive and a negative end. It therefore has a dipole moment and is said to be dipolar. This will have significant impact on the properties and behavior of these molecules.

1.3 Origin of the "Nonlinear Optical Effect"

The classification of the interaction between a material and impingent light as "nonlinear" implies that a linear response exists. Actually, all interactions between light and matter will have some nonlinear attributes, pointing to the somewhat obsolete use of the term linear. The nonlinearities of typically "linear" processes, such as birefringence and refraction, are just too small to be noticed or concerned with. If they were not, simple interactions, such as that between light and air, would have marked effects. A light bulb viewed through the air would appear to be more than one color and would move position if it's intensity changed, rather than appearing to get brighter.[1]

The focus of current nonlinear optical research is on the effect of an electromagnetic field of light energy on various materials, to produce new fields of altered intensity, phase, amplitude, frequency, or direction from the original quantity. The nonlinear optical effects we are concerned with arise from the relative polarization of the molecules.

1.4 Polarization of Molecules

Stucky et al[2] summarize, "any process is essentially nonlinear if the response to an input (the output) changes the process itself." The interaction of light with a molecule capable of nonlinear optical effects will cause the molecule's properties to change, and the light will now "see" a different material than the original photons did. A nonlinear effect is feedback that changes the operating characteristics of a closed loop system, where a molecule is the system. This occurs because the electron density in the molecule interacts, or is polarized, by the electromagnetic field of the light.

The electric field of light E, interacts with the electrons, of charge q, to produce a force qE that displaces or polarizes the electron. Pulling the electron density away from the nucleus results in an induced dipole, of moment μ, being formed. The displacement or polarization P, is proportional or linearly related to the electric field by:

$$POLARIZATION = P = \alpha E \qquad (1)$$

where α is the linear polarizability of the medium. This is simply based on the electrons being modeled as classically oscillatory in nature. The electric field affects all of the charged species in the molecule. Thus, if the molecule is dipolar it will expand and contract in shape on the axis of the dipole with the attractive and repulsive forces of the field.

An introduction into the anisotropic nature of polarizability will illustrate the significance of tensors to the discussion of nonlinear optics (NLO). The three dimensional shape of an electron is distorted not only in the direction of polarization x, but also in the y and z directions. In order to completely describe the polarization due to a field from the x direction, a term for each of the directional polarizations is needed. Since the field itself could also be from three directions, nine individual terms are necessary. The convention for describing all such quantities is tensor notation, derived from a system of matrices, in this case a 3 x 3 matrix. The proper notation for the linear polarization term is actually the polarizability tensor, α_{ij}, making the equation for linear polarizability:

$$P_i(\omega) = \sum_j \chi_{ij}(\omega) E_j(\omega) \qquad (2)$$

where $\chi_{ij}(\omega)$ is the linear susceptibility. The susceptibility, discussed below, is the bulk equivalent to α_{ij}, which describes a molecular quantity.

The discussion above is based on the assumption that the linear displacement of the charge is based on a classical harmonic oscillator, with the restoring force linear to the displacement and the frequency of oscillation of the electron matching that of the impingent light. However, this assumption is not satisfactory at explaining polarization under all circumstances.

1.5 Nonlinear Polarization Terms

In reality, the response of the molecule to the light is not linear at all. The electron density in these chromophores is more highly concentrated in the vicinity of atoms that are more electronegative. The electrons' oscillation frequency does not match the original frequency of light. The induced polarization has its own internal electric field that modifies the light's electric field and subsequent polarization. This is the basis of the nonlinear effect. A Taylor series expansion for the resultant second-order NLO polarization can be written:

$$P=\mu_0+\alpha_{ij}E_j+\beta_{ijk}E_jE_k+\gamma E_jE_kE_l+\ldots \qquad (3)$$

It is the terms beyond αE that are the nonlinear terms and give rise to a nonlinear effect. Equation (3) holds true when the field strength is small and the frequency of the light is non-resonant. The term ß is most important to our design considerations and is known as the molecular hyperpolarizability. If the term is used to describe a collection of molecules, for instance in a solution or polymeric matrix, it is described as the susceptibility χ. The susceptibility is similar to the molecular quantity but relating the two exactly requires considering the value of the internal fields and their propagation characteristics.[3] This exact relationship is beyond the scope of this paper but a significant amount of research has been done relating the two quantities.[4(a)-(f)] The primary design consideration in the synthesis of molecules is still ß because it is readily measured and is a good indicator of what the bulk characteristics of the medium will be. The equation for the overall polarization of a medium is then:

$$P=P_0+\chi^{(1)}E+\chi^{(2)}E^2+\chi^{(3)}E^3+\ldots \qquad (4)$$

P_0 is the polarization of the molecule due to its internal dipole moment, and the remainder of the polarization is induced by the external electric field of the light. Equation (4) is relevant to the energy levels we are considering because it applies to power levels on the order of kW/cm^2 to

MW/cm^2. The molecules will be used in applications with visible light lasers which have power levels of this magnitude.

1.6 Examples of Nonlinear Processes:

Second Harmonic Generation

What are the observed characteristics of a material that exhibits a nonlinear optical effect? For our purposes, one of the most relevant effects that can be produced is second harmonic generation (SHG) or frequency doubling. It is being used in a large variety of devices and applications (see Chap. 2) and the potential future uses are also very promising. The origin of SHG can be shown by a variety of methods ranging from trigonometric arguments[5] to a more complex solution of Maxwell's equations.[6]

As we earlier stated, an effect of linear polarization is to induce an oscillation of the individual dipoles in the molecule at a frequency ω corresponding to the frequency of the incoming light. They will re-emit radiation of the same frequency and therefore the light will pass unchanged. In nonlinear materials, the polarization of the medium was described above in Equation (4). If we substitute $E_0\cos(\omega t)$ into this equation for the sinusoidal electric field, and use trigonometric identities, we see that the polarization equation becomes:

$$P=(P_0+\frac{1}{2}\chi^{(2)}E_0^2)+\chi^{(1)}E_0\cos(\omega t)+\frac{1}{2}\chi^{(2)}E_0^2\cos(2\omega t)+\ldots \tag{5}$$

This equation actually describes two significant NLO processes. The first term is a direct current, static electric field contribution to the polarization. This illustrates that light hitting the medium will also produce an electric field. This is known as optical rectification and has been measured on inorganic crystals[7] but no organic media. The other terms in the equation are the incident light frequency (ω) and the frequency-doubled term (2ω), respectively. This frequency-doubled term is the origin of SHG. It is apparent that a nonlinear material exhibiting SHG will produce light of half the incident wavelength. The first example of any optical nonlinear effect ever observed was in 1961, by Franken and co-workers when they doubled the frequency of a ruby laser (694.3 nm) into the ultraviolet region (347.15 nm).[8]

The origin and characteristics of the processes associated with nonlinear optics have been introduced. We have described the molecular attributes that are necessary for a hypothetical compound to exhibit these types of behavior, but they are obviously not measurable by any means. Empirical methods for determining the usefulness of various compounds exist and are developing to meet the demand for techniques sensitive to a particular class of materials.

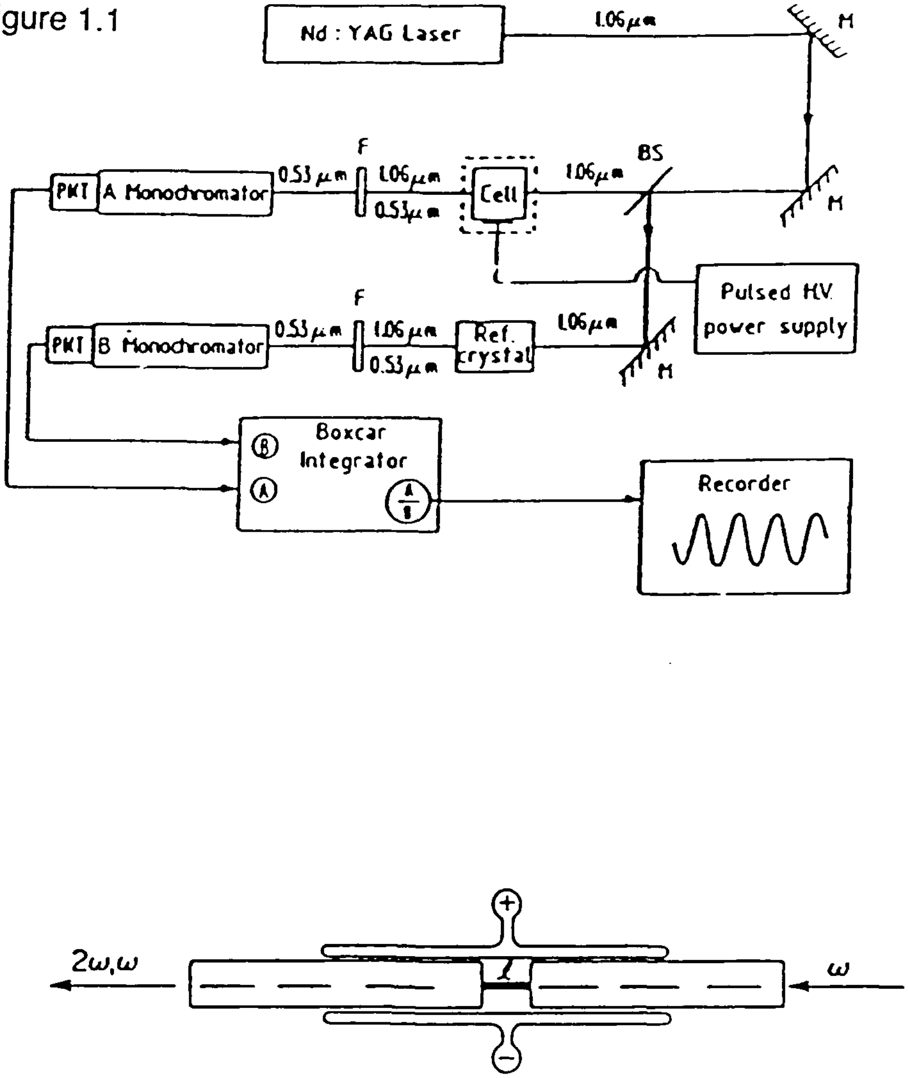
1.7 Description of the Electric Field Induced Second Harmonic Generation Experiment

In 1975, B. F. Levine and C. G. Bethea[9] developed the technique of electric field-induced second-harmonic (EFISH) generation to measure the hyperpolarizability ß of molecules from measurements on liquids or solutions. The main advantage to this technique is that it can be applied to solutions. It also provides a measurement of ß without the necessity of crystallizing the molecules into a noncentrosymmetric structure. The noncentrosymmetric arrangement is obtained by applying a strong DC electric field across a solution of the dipolar molecules.

Figure 1.1 depicts the essential elements of a standard apparatus for the EFISH experiment.[10] In this example, the light source, a 1.064 μm Nd^{+3}:YAG (yttrium-aluminum-garnet) laser, is split into two beams; one beam is directed into the sample cell and the second is a reference beam. The reference beam is directed into a matrix which contains a material whose second harmonic signal is known, such as quartz or $LiNbO_3$, and can be compared to the sample's signal to account for variations in the input beam intensity. Filters and monochromators are used to filter out the incident fundamental frequency before it enters the detectors, so that only the second harmonic is detected.

Although, in principal, the experiment is straightforward; in practice, there are many experimental and

Figure 1.1



"Organic Polymeric and Non-Polymeric Materials with Large Optical Nonlinearities", D. L. Williams, *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 690-703 computational difficulties. For example:

(a) in order to minimize problems associated with electrolysis of the solute or polarization of the cell, a pulsed high-voltage source is used which can generate dc pulses in the 0 to 10 kV range;

(b) the lens design which focuses the beam onto the sample must take care to avoid divergence of the beam in the cell and stay below high powers or intensities where self-focusing effects can occur;

(c) the measurement of signal intensity at 2ω as a function of path length is then needed because of phase mismatch between the fundamental and harmonic waves propagating through the medium.

Second harmonic generation is a phase sensitive process; that is, the transfer of energy between a fundamental and harmonic wave depends on the phase relationship between the two. This variation of signal intensity as a function of path length Δl is handled by measuring the path length variation induced by a translational move of the sample cell Δx. The relationship between the two is:

$$\Delta l = \Delta x \tan\alpha \qquad (6)$$

Alpha is the angle between the walls of the cell containing the sample. The need for this geometric calculation and measurement is primarily based on the fact that the harmonic intensity which is being collected is measured as a function of position.

The sample cell design should be elaborated upon because it has significant impact on the efficiency and accuracy of the apparatus. The cell consists of two glass rectangles about 3 mm thick and 1 cm long set at an angle α with respect to each other. Electrodes are placed above and below these glass surfaces which are extended to about five times the gap spacing to avoid non-uniform electric fields at the glass-liquid interface. The electrode should also be much wider than the Δx distance covered as the cell is moved. The gap in between the glass is about 1 - 2 mm and provides for easy cleaning and sample addition and removal.

The quantity for β is obtained from manipulation of experimental measurements of second harmonic light. The value for β that is obtained is in esu units. Typical values for organic materials are in the 10^{-30} esu range.

1.8 Molecular Characteristics for Exhibiting NLO Effects

Having introduced both the origin of a nonlinear optical effect and some processes which utilize this effect, we have demonstrated some properties of targets that would be desirable to have. We must now answer the question, what types of molecules will exhibit SHG or other desired NLO effects?

Polarization of the molecule involves the displacement of electron density in the molecule. This is one of the more important factors in considering what type of molecule would be optimum for SHG. If the system is a conjugated organic system, there is a high degree of π electron delccalization and this makes it more likely for the electron density to be displaced. A high degree of conjugation also correlates with absorbtion of light at longer wavelengths and higher molar absorptivities. The degree to which conjugation is advantageous is not unlimited however; beyond 20 adjoining double bonds,[11] the benefit of additional conjugation is small compared to losses in stability and rigidity.

Since it is asymmetric polarization that yields NLO effects, the materials or molecules creating such an effect must not have a center of symmetry. A centrosymmetric molecule or medium will have a susceptibility $\chi \approx 0$.

A noncentrosymmetric arrangement of molecules must be achieved either by crystallization, or some other means. For certain types of molecular systems, it is possible for the molecule to be oriented by an electric field. To be efficiently oriented by an electric field the molecule should be highly dipolar, and rigid, that is, not prone to molecular flexing, bending, or twisting conformations. This is necessary so that the direction of polarity remains constant relative to the geometry of the molecule. The molecule should also be rod-shaped in order to be efficiently packed together when aligned, achieving high number densities.

Another factor that has a significant influence on the usefulness of a molecule as a NLO material is the substituent type on the conjugated system. As stated above, polarization causes asymmetrical charge distribution and therefore if the molecule already exists in a substituent-induced asymmetrical charge state as in Figure 1.2, it is more likely to generate a high value of β. Many experiments have been done to describe and characterize the effect of different substituents,[12] as well as empirical calculations to predict the same.[13] The most important finding that we applied in our research was the requirement that one end of the molecule be electron rich and the other electron poor.

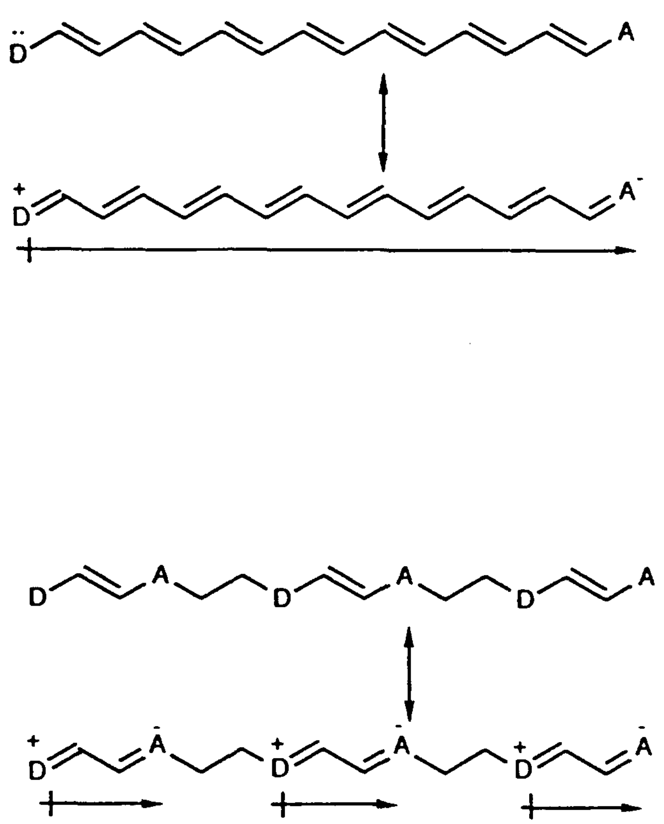
1.9 Some Methods for Obtaining a Noncentrosymmetric Arrangement

For the purposes of this discussion, we will consider four methods of obtaining a noncentrosymmetric arrangement of molecules. These are crystal growth, poled polymer systems, monolayer assemblies,[14] and orientation in a diblock copolymer.

The advantages of crystalline materials are (1) their dense packing structure and (2) their highly specific and constant arrangement of molecules. The density is advantageous because the bulk susceptibility, $\chi^{(2)}$, is directly proportional to the density of the material. The specificity provides a high level of $\chi^{(2)}$ also, because if desired molecular geometrical arrangements are known, and are obtained, they can be kept constant and then shaped or cut

Figure 1.2

General Structures of Dipolar Molecules



into required configurations. Most current laboratory use of NLO materials as frequency doublers for high-powered lasers utilizes crystals. The drawbacks are that organic crystals are usually very difficult to grow in large sizes, structurally unpredictable, easily degraded by heat and light, and fragile. There has been little success in getting crystals in the optimum structural arrangement.

Poled polymers represent an encouraging area of development. This technique usually involves attaching the NLO chromophore on a polymeric backbone as a side chain, and then poling the matrix with an electric field. Solvent-coated polymers are very easily manufactured into thin, planar films and are well suited to use in waveguide devices. There is great flexibility in what constituents can be used and therefore optimum designs can be realized. The main disadvantage to the use of any type of polymer is that the poling process can be arduous and complex. Some other hurdles are dilution of the chromophore in an acceptable matrix and orientational instability of the medium after electric field poling.

The monolayer techniques may offer the greatest orientational stability, ease of processibility, and design flexibility of the three methods. Marks et al[15] have investigated an alternative method of aligning monolayers demonstrating NLO characteristics, utilizing covalently-linked self-assembled multilayer structures. The Langmuir-Blodgett technique[16] is another, well-practiced method of monolayer construction. This method involves layer-by-layer assembly of randomized, amphiphilic monomers onto a substrate off the surface of water into closely-packed, oriented arrays. The layers are stabilized by simple Van der Waals forces or by reactive substituent groups. Since the method allows rigid control over layer thickness, it has the potential for application in devices where phase matching is a vital consideration. Langmuir-Blodgett films however, are slow and difficult to make due to the fact that they are deposited one layer at a time. There has also been little success in developing a material with this technique that remains stable under slightly rigorous conditions. All of the applications involving nonlinear optical devices will require that the material be able to withstand the environment that the device operates in and be able to perform its function; thus, a simple, more durable orienting technique would be an attractive alternative.

My research effort focused on the synthesis of organic materials exhibiting desired optical responses, in the hope of developing materials for application(s) in photonic or electrooptic devices. The synthesis involved three different classes of NLO materials. The first was an amphiphilic azo dye that is to be utilized in a novel, alternative polymer assembly technique, called di-block copolymers. Diblock copolymers are an example of a way of partitioning target molecules at a phase boundary, similar to Langmuir-Blodgett methods, except the "phase" is one region of the polymer. The second project was the synthesis towards an example of a conjugated polymer which has unique conductive properties. They might have the potential application of acting as a molecular-scale switching device. The third area of concentration was the synthesis of a poly(imine) polymer that demonstrates the ability to combine dipolar monomer fragments into oligomers which conserve the net additive dipole moment.

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Chapter 2: Applications in Nonlinear Optics

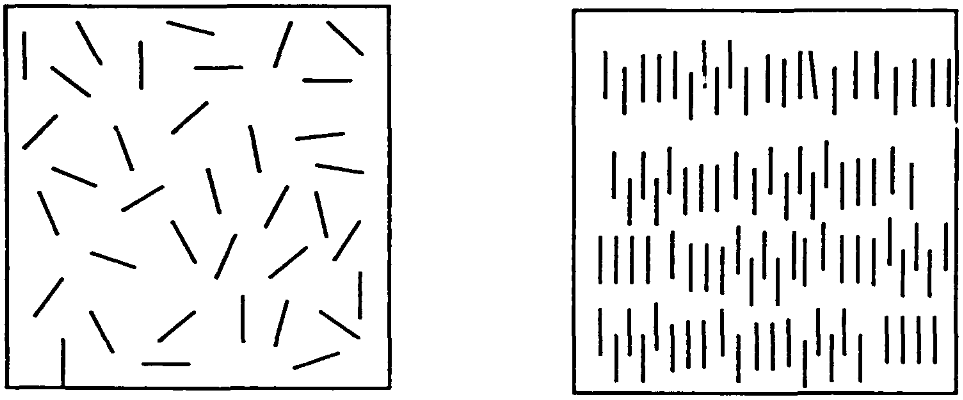
2.1 Liquid Crystals

Liquid crystals have a wide range of interesting physical properties, and present many possibilities for use in optical and electrical applications.

A liquid crystal is a fluid material composed of rod-like molecules possessing order over a short-range.[1] The material lacks the long-range order characteristic of crystalline solids, but contains small volumes in which molecules may be present in ordered domains. Generally, three classes of liquid crystals are considered. The first, and simplest type is the nematic phase, in which the molecules show an end-to-end orientation on average, but the centers are randomly distributed. The second class is the smectic phase in which the molecules are ordered and the centers tend to lie in layers. Within the layers, however, the centers are randomly distributed (see Figure 2.1 for diagram of these two phases). The third phase, cholesteric, shows ordering of rods and centers within two-dimensional layers, but the directional orientation varies from layer to layer along the third dimension.

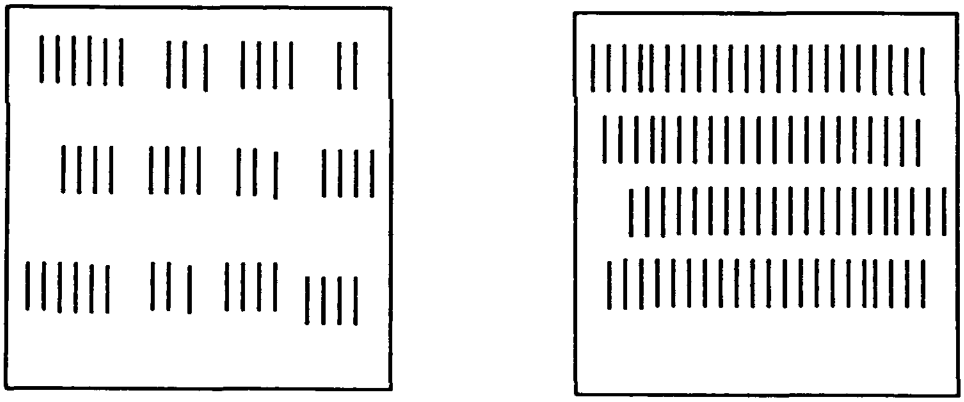
Their interesting structure gives them useful physical properties that have been exploited in many technological applications. In the 1930's, E. H. Land developed a light polarizing material in which tiny, oriented solid crystallites were suspended in a clear liquid-like polymer.[2] In this

FIGURE 2.1 STATES OF STRUCTURAL ORDER



LIQUID

NEMATIC PHASE



SMECTIC PHASE

MOLECULAR CRYSTAL

ADAPTED FROM: OXTOBY, D. W.; NACHTRIEB, N. H.; FREEMAN, W. A. "CHEMISTRY: SCIENCE OF CHANGE", SAUNDERS COLLEGE PUBLISHING: PHILADELPHIA, 1990, P. 874.

material, the refractive index of the polymer was matched to one of the principal refractive indices of the crystallite material. Thus, the material acted as a light polarizer, passing one component of polarized light and scattering the other. This marked the birth of liquid crystal optical applications. There are many other more recent examples. For example, the displays in digital watches and calculators rely on the sensitivity of the crystal to small electric or magnetic fields; their use in thermometers is due to phase changes as a function of temperature. Other applications are being investigated that use their unique optical and piezoelectric features. For example, liquid crystals possess small Young's moduli relative to solid crystals; thus, they produce a substantial voltage upon small mechanical deformation. Due to this, their use as piezoelectric transducers is being investigated.[3] Also, liquid crystals are being utilized in optical applications such as light shutters for optical signal processing, flat-panel TV screens, and switchable windows.[4]

2.2 Optical Data Storage[5]

The storage of digital information by optical methods has found widespread consumer use in the form of audio compact discs (CD's). The data, in this case the coding for music, is stored on the surface of a polymer by engraving or embossing small holes in a polymer surface. The polymer surface is then covered with a thin film of metal and the data can be read with a low-power, focused laser beam. Most of the current optical discs are read-only-memory (ROM) type because the holes cannot be erased. Since most data storage applications require the ability to read and write data, it would be of great use to be able to perform both of these functions on an optical disc. The use of optical data discs has advantages over the magnetic storage devices currently used: (a) they are not sensitive to surface damage or dust particles, and (b) they are generally more durable and last longer. One area of improvement that is needed is to increase the density of data storage that is possible.

A chromophore capable of second harmonic generation would find direct application to the field of optical data storage. The density of the data storage on all optical storage systems is limited by the wavelength of the laser being used to "write" the data onto the polymer substrate. This is because the size of the smallest spot or pit that can be embossed is equal to the wavelength of the laser light. The density of data that can be stored is given by the equation:

$$Density = (A/\lambda)^2 \qquad (7)$$

where A is the aperture of the lens focusing the laser beam and λ is the wavelength of the laser. A chromophore that could double the frequency of the laser, thus halving the wavelength, would enable four times as much data to be stored in the same size space.

The use of frequency doubling for data storage has already been demonstrated with 473 nm light from a GaAlAs laser[6]. The development of more efficient nonlinear optical materials for frequency doubling will lead to more compact, higher-density optical data storage devices.

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Chapter 3: Synthesis of Azo Dyes

3.1 Introduction

The acid-base indicator commonly known as p-methyl red is an extended, donor / acceptor substituted azo dye. The chromophore in this molecule is appropriate for second harmonic generation. Our goal in this project was to prepare analogues of this molecule suitable for orienting at the interface of two immiscible phases.

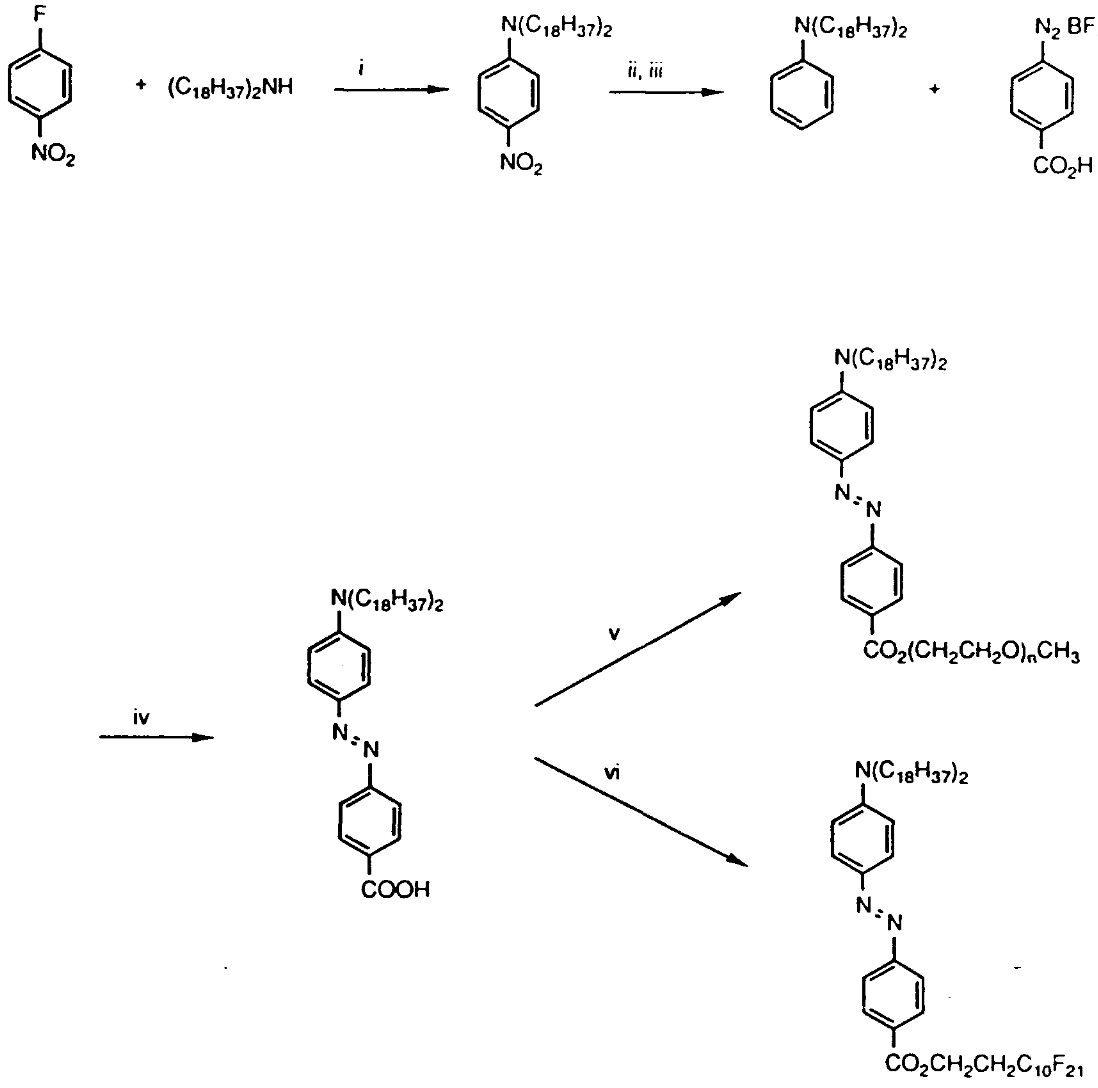
The two targets, shown in the synthesis in Figure 3.1, have a lipophilic dialkylamino chain on one end and either a polyethylene glycol or a fluorocarbon chain on the other. These molecules as a whole are referred to as "amphiphilic."

Our hypothesis is that these targets will partition themselves at the phase boundary between the lipophilic and hydrophilic layers of a diblock copolymer[1]. It has been demonstrated that a diblock copolymer of poly(methylmethacrylate) and polystyrene will organize into microdomains of ordered lamellae when an electric field is applied[2]. It is our expectation that the target molecules will align themselves at the interface of these layers so that the chromophores may be used in a frequency doubling experiment.

3.2 Synthesis

Preparation of the two target esters was envisioned to occur via the corresponding carboxylic acid, which in turn should be obtained from an azo coupling of the dialkylaniline

FIGURE 3.1
SYNTHESIS OF AZO DYES



i. triethylamine, acetonitrile, reflux; ii. 10% Pd/C, cyclohexene, ethanol, reflux; iii. hypophosphorous acid, HCl, sodium nitrite, ethanol, water; iv. acetic acid, 5-10 deg. C, then warm to room temperature; v. 1 eq. DCC, 1 eq. DMAP, 1 eq. poly (ethyleneglycol)-monomethylether, methylene chloride; vi. 1 eq DCC, 1 eq. DMAP, 1 eq. 1H,1H,2H,2H-perfluoro-1-dodecanol.

and 4-benzenediazonium carboxylate.

The dioctadecylaniline was prepared using the procedure previously reported[3] by Katz et al: dioctadecylamine was reacted with 4-fluoronitrobenzene to give the nitroaniline derivative; subsequent nitro group reduction, either with tin metal or by transfer hydrogenation, and hypophosphorous acid deamination, gave the dialkylaniline.

Coupling of this aniline with 4-benzenediazonium carboxylate initially presented some problems. Early attempts at preparing the diazonium ion in aqueous solution, in the presence of dioctadecylaniline, led to only small amounts of coupling product, presumably because of solubility problems. This problem was solved by preparing the diazonium ion as its tetrafluoroborate salt.[4] The salt could be coupled efficiently to dioctadecylaniline in acetic acid solution to yield the desired azo acid.

To form the fluoroester, the acid was combined with dicyclohexylcarbodiimide (DCC), dimethylaminopyridine (DMAP), and 1H,1H,2H,2H-perfluorododecanol[5]. The product was purified on a silica gel chromatography column, eluting with ether.

To form the polyethylene glycol (PEG) ester, the analogous esterification was run using poly(ethylene glycol) methyl ether. Unreacted alcohol, and DMAP, were removed by washing the mixture with a dilute aqueous HCl solution. The product was purified on an alumina gel chromatography column using acetone as eluent.

TLC analysis of the crude PEG ester suggested that the product could be purified by chromatography on silica gel eluting with methylene chloride or chloroform. These combinations were attempted, but the product could not be recovered from the column. It is unclear why the TLC results on these molecules were not transferrable to column chromatography.

Because of the purification difficulties initially experienced, an alternative esterification sequence was investigated. The acid was converted to the acid chloride and then reacted with one of the respective alcohols to yield an ester. This process was underway, but was abandoned in favor of the above reaction when the purification problem was solved.

3.3 Results and Discussion

The visible spectrum of the esters was obtained to determine the extent to which the molecules existed in solution in the extended geometry. This was important because the usefulness of the chromophore would be doubtful if there was significant twisting or folding of the long ends of the molecule. The relative shifts in λ_{max} observed were quite small (see Figure 3.2 and 3.3), which supports the conclusion that the molecules exist in the desired extended arrangement.

The ^1H NMR of the esters presented some unexpected and interesting results. In the azo acid, Figure 3.4, the expected four doublets are observed for the four pairs of

Figure 3.2
UV- Visible Absorbance Spectrum of Fluoroester in Various Solvents

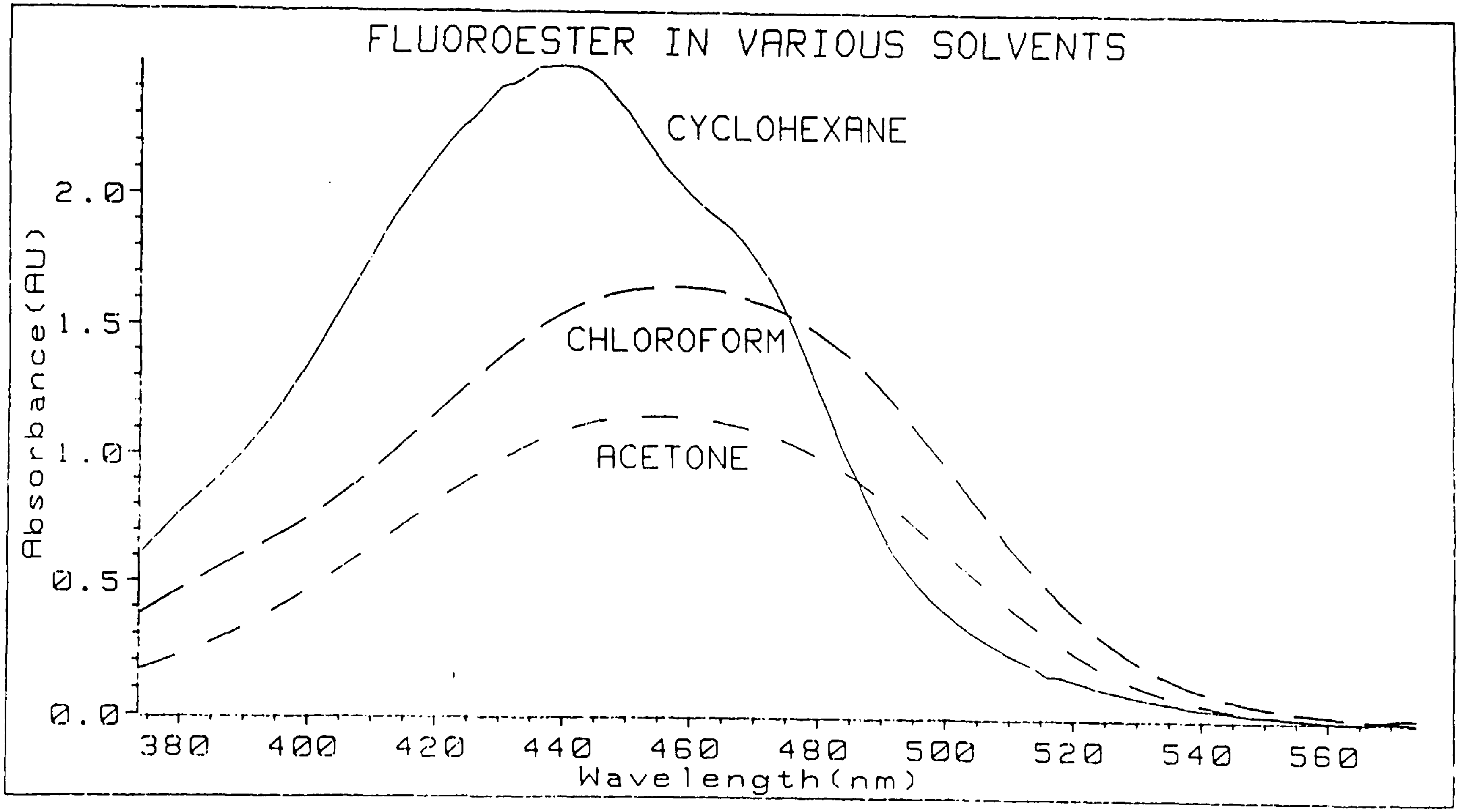


Figure 3.3
UV- Visible Absorbance Spectrum of PEG Ester in Various Solvents

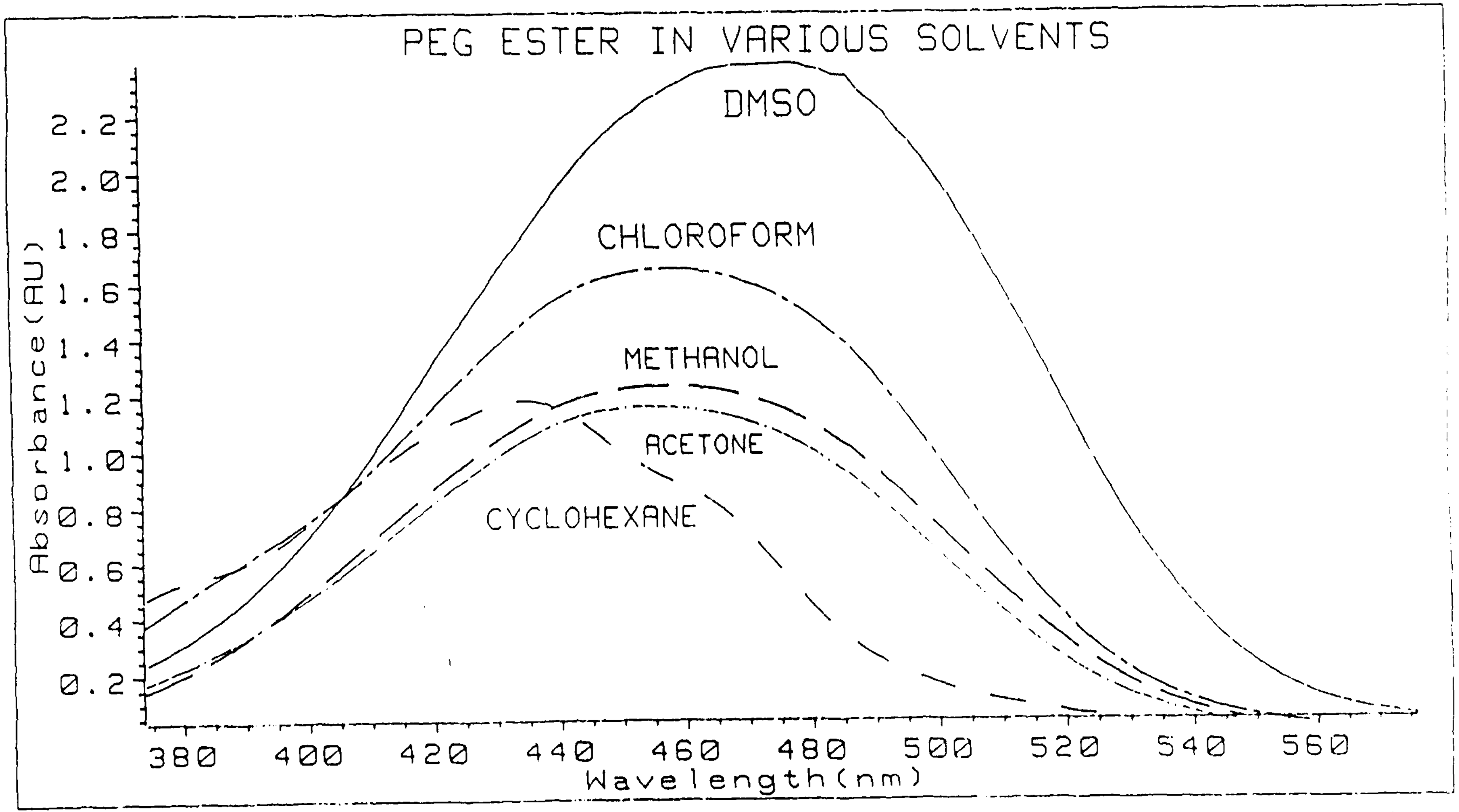
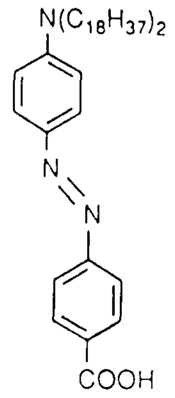
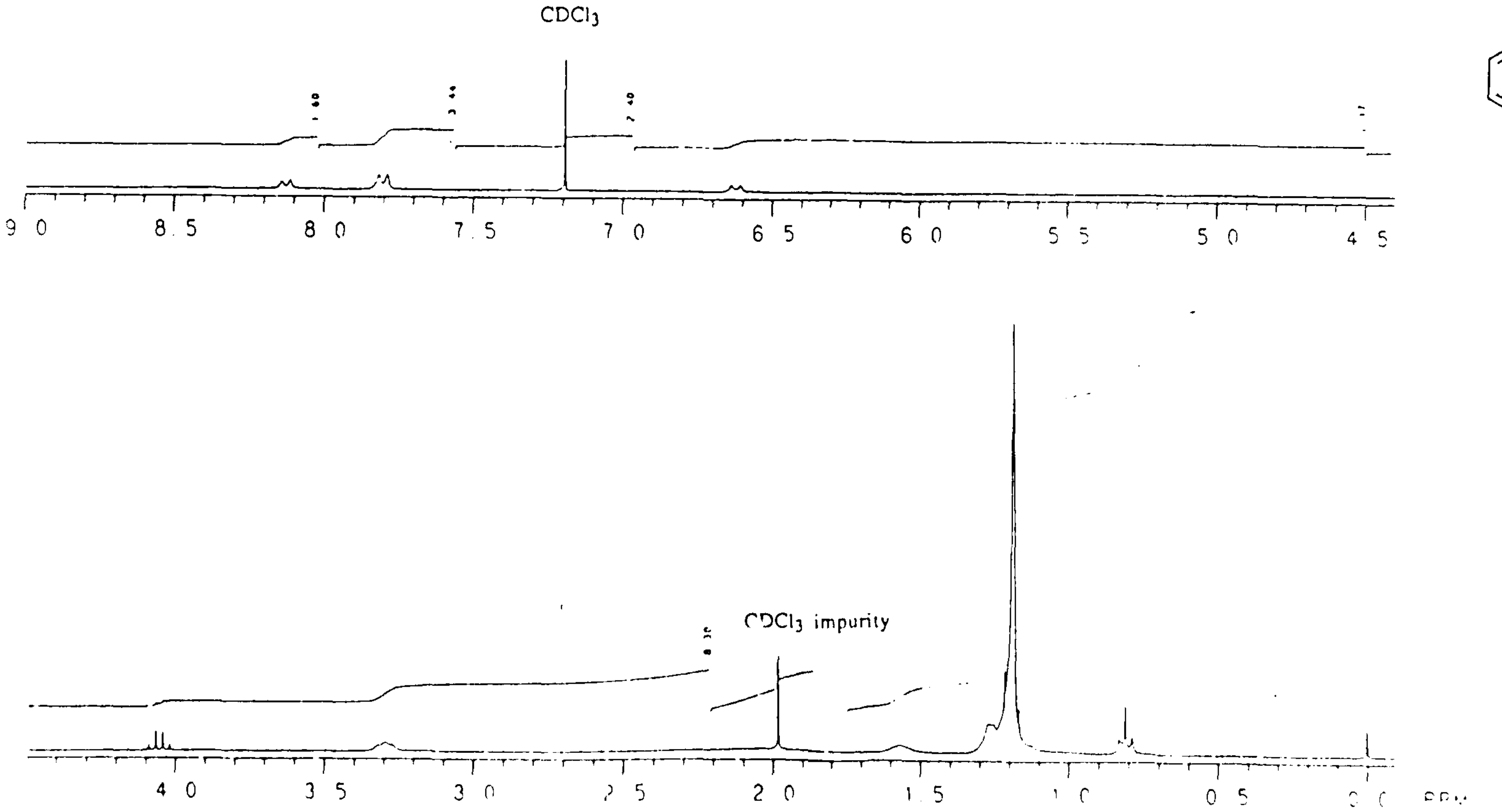


Figure 3.4
NMR of Azo Acid

Aromatic Region Signals:
8.1 ppm doublet, 2H (ortho to carboxylic acid group)
7.8 ppm doublet, 4H (ortho to azo nitrogens)
6.6 ppm doublet, 2H (ortho to aniline nitrogen)





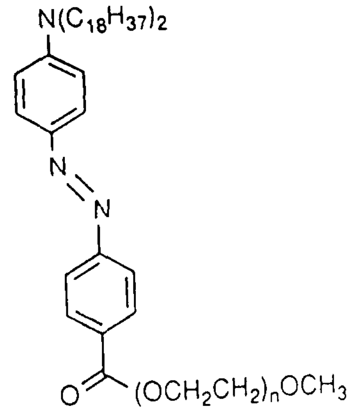
aromatic protons. The PEG ester, Figure 3.5, displays a similar aromatic region.

However, the fluoroester NMR, Figure 3.6, shows five distinct aromatic signals. Our initial interpretation was that the two protons adjacent to the carbonyl are no longer equivalent due to the rotation of the aromatic ring / carboxylic ester bond being inhibited by the size of the fluoroester tail. This explanation is dissatisfying to us for two reasons. First, the fluoroester tail is not substantially larger than the PEG ester, yet only the fluoroester shows the anisochrony. Second, the multiplet that is split into two signals is the most upfield of the aromatic's resonances; this signal should probably be assigned to the protons adjacent to the dialkylaniline nitrogen. While the extraneous signals may be due to some impurity, the free acid from which the esters are made appears to be clean; the source of the impurity is not apparent.

Approximations of the spatial arrangement of both esters were produced using the modeling program Alchemy™ (Figures 3.7 and 3.8). It can be seen that the dialkyl chains give the molecule a "T" shape, which is not the ideal molecular geometry. It is desired to have molecules that are as linear and rod-shaped as possible in order to obtain efficient close-packed arrangements. A synthetic target with the lipophilic end consisting of a single alkyl chain substituted on a piperidine ring, modeled in Figure 3.9, represents a more

Figure 3.5
NMR of PEG Ester

Aromatic Region Signals:
8.15 ppm doublet, 2H (ortho to carbonyl)
7.8-7.9 ppm two doublets, 4H (ortho to azo nitrogens)
6.7 ppm doublet, 2H (ortho to aniline nitrogen)



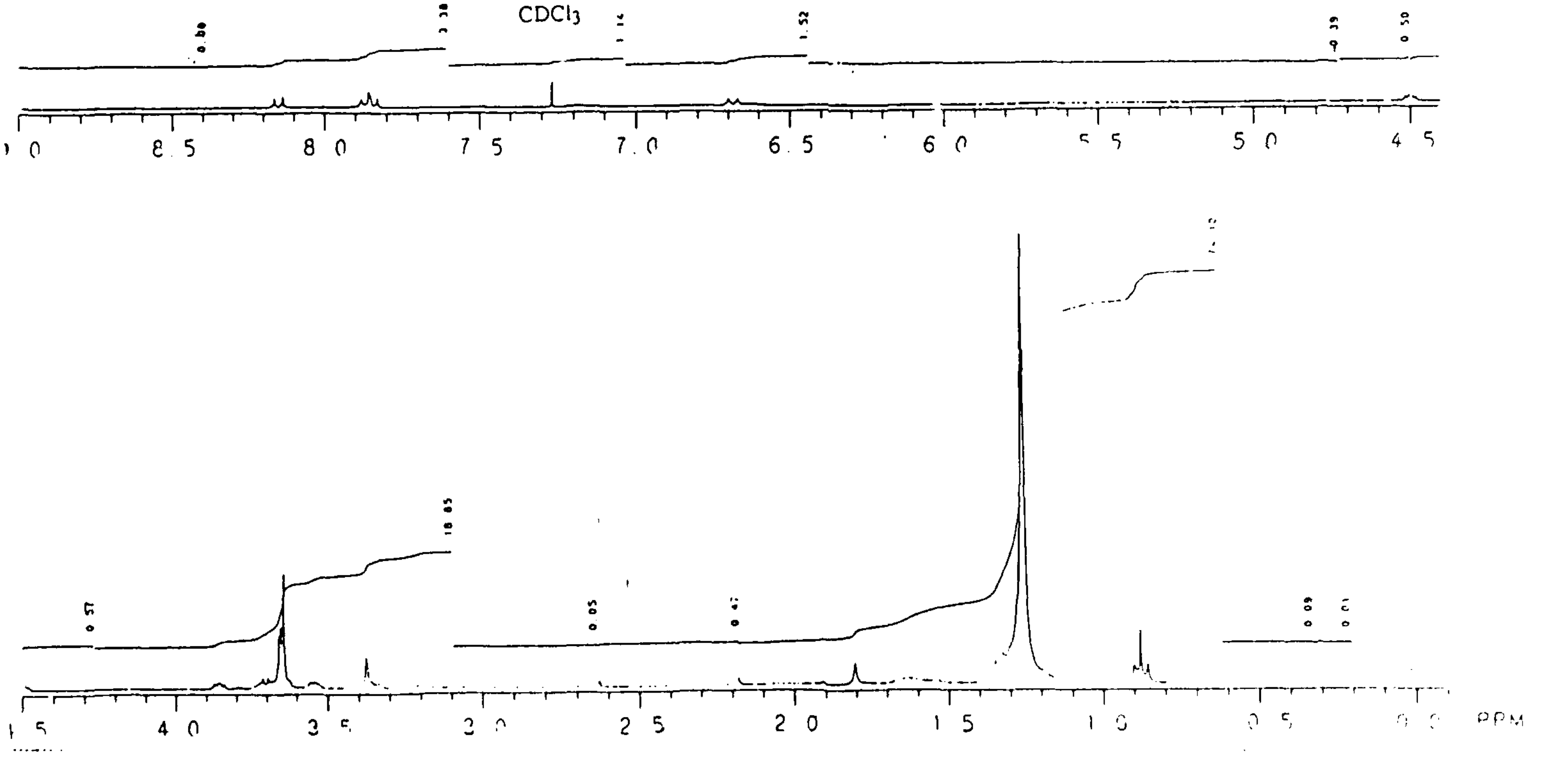
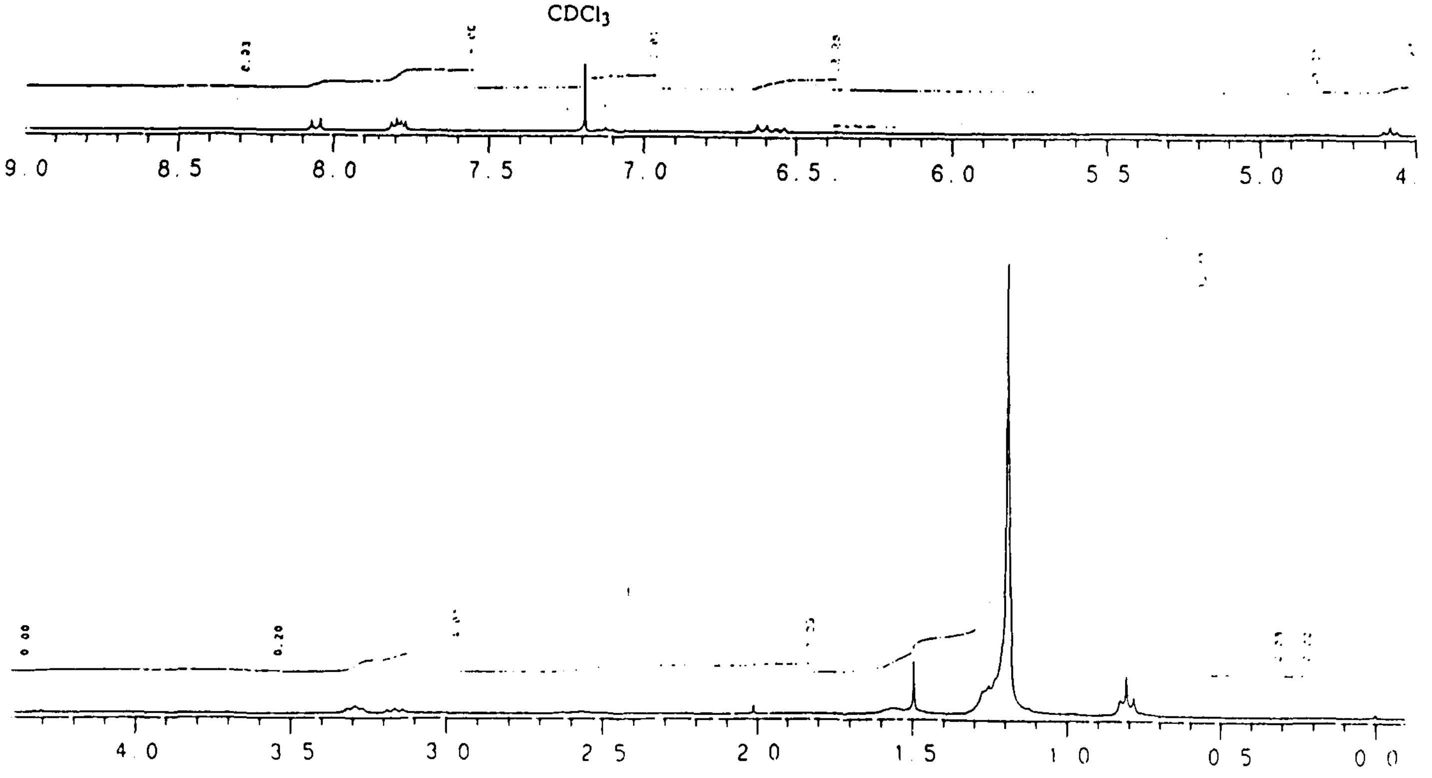
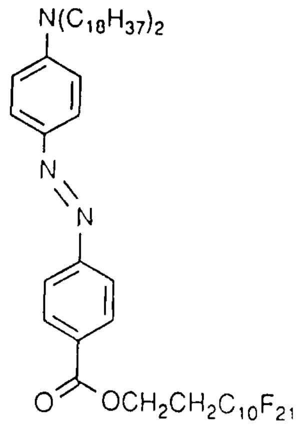
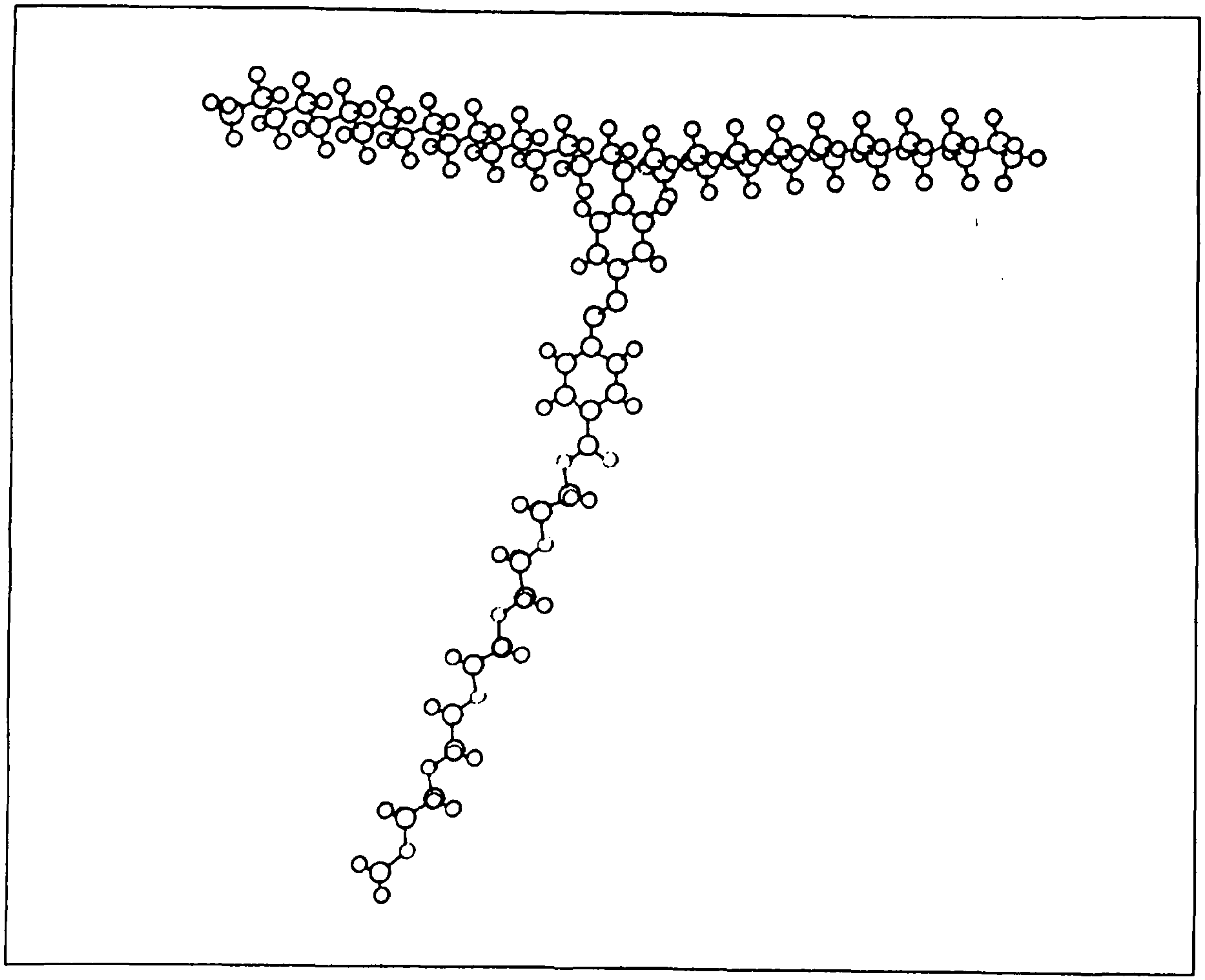


Figure 3.6
NMR of Fluoroester

Aromatic Region Signals:
8.05 ppm doublet,.2H (ortho to carbonyl)
7.8 ppm two doublets, 4H (ortho to azo nitrogens)
6.65-6.5 ppm two doublets, 2H (ortho to aniline nitrogen)

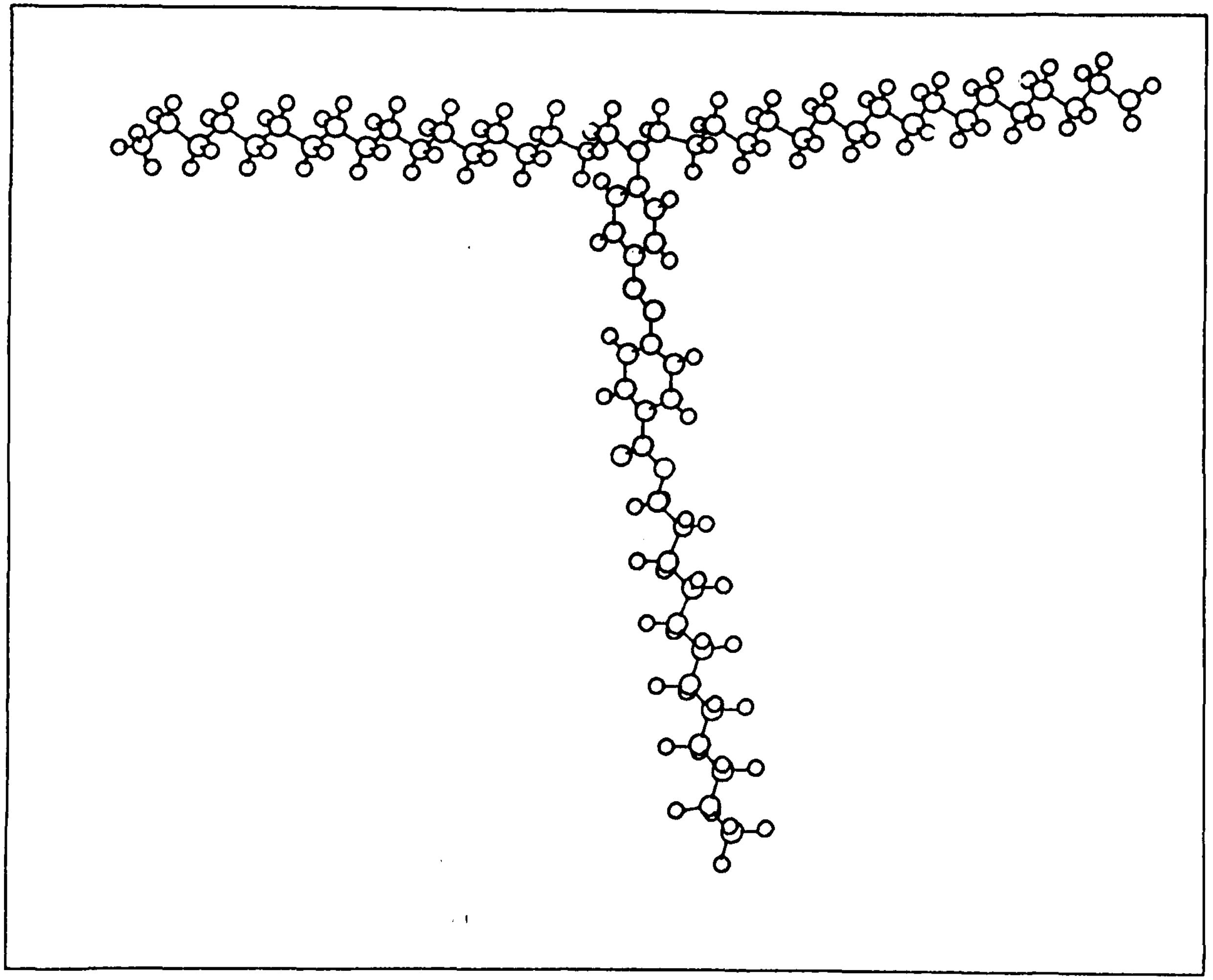






Alchemy II
TRIPOS Associates
St. Louis, Mo.

Figure 3.7 Alchemy Plot of the Approximate Geometry of the PEG Ester



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St. Louis, Mo.

Figure 3.8 Alchemy Plot of the Approximate Geometry of the Fluoroester

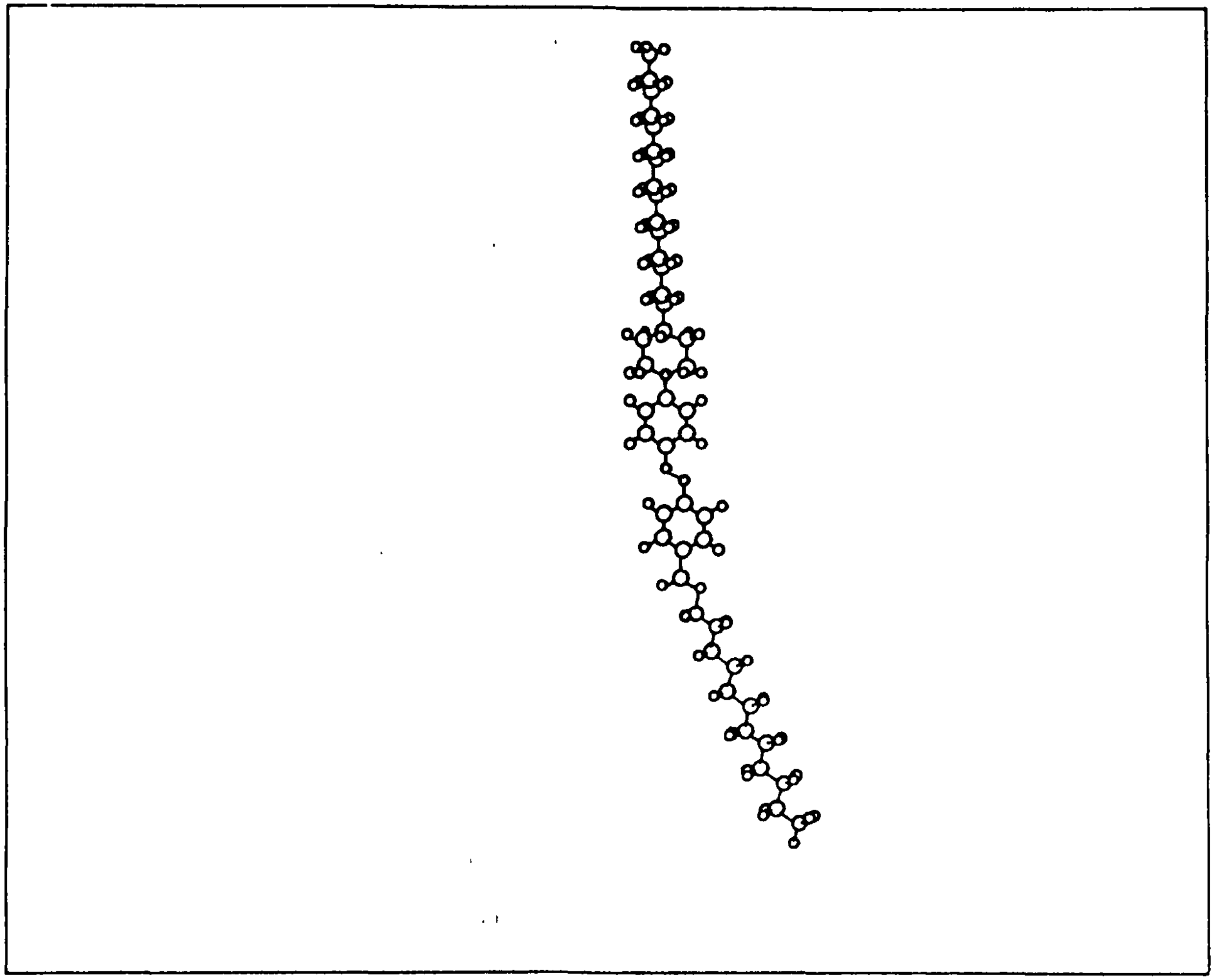

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Figure 3.9 Alchemy Plot of the Approximate Geometry of a Synthetic Target desirable possible target.

The second harmonic generation and interfacial alignment studies have not been carried out yet.

Chapter 3 References

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Chapter 4: Synthesis of Polypyridine Vinylene

4.1 Introduction

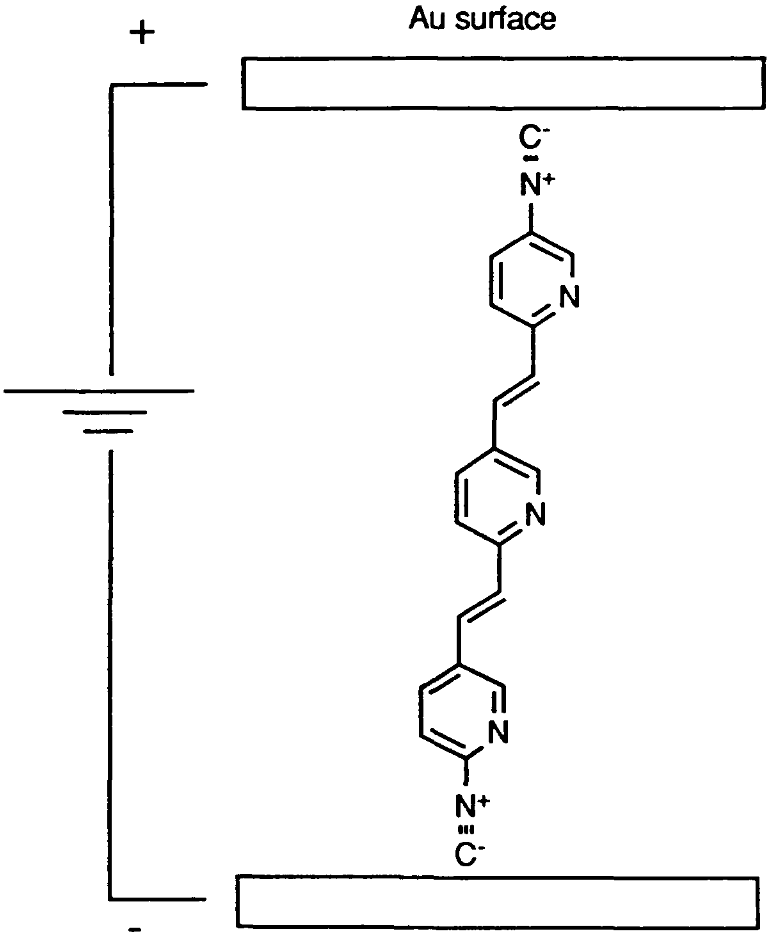
One category of targets in nonlinear optics focuses us on the synthesis of the class of molecules known as conducting polymers. A conducting polymer has an extended π-conjugated system along the polymeric chain that allows it to pass electrical current; examples include polyanilines, polythiophenes, polypyrroles and related molecules. In some ways it is useful to think of such materials as "molecular wires"[1].

These materials are postulated to be useful in a variety of applications: as an active electrode in a rechargeable electrode; as a "smart window" which changes color with changes in temperature or electric charge; as a diode device[2].

Their potential use as a current-rectifying diode is of primary interest in this research. If a polarized polymer were synthesized having a functional group on each end that could be placed on an electrode across an electric field, the molecules could be aligned and would serve as a bridge between the surfaces (Figure 4.1). Since the molecule is polarized, it would conduct electricity preferentially in one direction, thus acting as a switch between the surfaces. From a material science or engineering point of view, this is an optimum size and functional ability; these molecular diodes could be the next generation of circuit chip switching devices.

The particular polymer of interest in this report is a polypyridine vinylene.

Figure 4.1



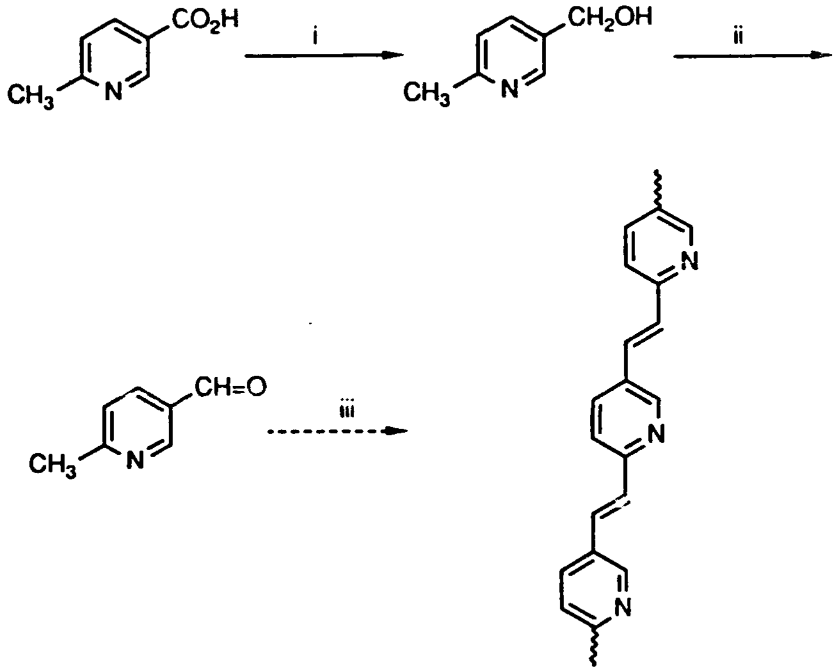
4.2 Attempted Polymer Synthesis

In the retrosynthetic analysis of the target polypyridine vinylene, a large number of approaches seemed reasonable. In trying to reduce the number of synthetic routes to a minimum, a principle concern was that the synthesis be entirely regiospecific; there should be no possibility of incorporating any pyridine units aligned in the wrong direction with respect to the polymer backbone. The strategy eventually pursued was based on the aldol reaction. 2-Methyl and 4-methylpyridines are both known to undergo condensation reactions with carbonyl compounds under a variety of base promoted conditions, and methylquinolines and isoquinolines are reported to condense with aromatic aldehydes under acid catalysis[3]. Our hypothesis was that the desired polymer might be available by the self-condensation of 2-methylpyridine-5-carbox-aldehyde.

The starting point for the synthesis (Figure 4.2) was the commercially available 6-methylnicotinic acid. The acid was reduced using BH_3/THF[4]. A variety of different reaction scales were attempted and various yields were obtained; maximum yield was obtained when a one gram sample of acid was reduced with a two to three-fold excess of borane added in one portion. Larger amounts of borane-THF complex caused purification problems; considerable amounts of 1-butanol contaminated the pyridine alcohol. To remove unreacted acid from product 2-methyl-5-hydroxymethylpyridine, chromatography on a silica gel column eluting with ethyl acetate was

Figure 4.2

Polypyridine Polymer Synthesis



i. BH_3, THF; then, aqueous NaOH; ii. pyridinium chlorochromate, methylene chloride; iii. lithium diisopropylamide, THF effective.

After purification, the alcohol was oxidized to the aldehyde. Swern oxidation[5] was first attempted but gave very low yield in our hands. Alternatively, pyridinium chlorochromate (PCC) was investigated[6]. Again, however, only low yields of aldehyde have been obtained so far.

Although the aldehyde was obtained in low yield, proton NMR spectroscopy showed the product to be quite pure. In addition to the methyl and aldehyde singlets, the characteristic coupling pattern for the aromatic nucleus was readily observed.

Polymerization of the aldehyde was attempted by a variety of methods. Initial attempts at polymerization were carried out under Lewis acid conditions. There is some precedent that these reactions might be successful[7]. For instance, 4-methylquinoline, 1-methylisoquinoline and 3-methylisoquinoline all react with benzaldehyde in the presence of anhydrous zinc chloride to give the corresponding alkene; presumably, zinc chloride complexes with the pyridine nitrogen to generate an enamine which reacts with carbonyl compound.

The attempted self-condensation of 2-methylpyridine-5-carboxaldehyde with anhydrous zinc chloride in toluene was carried out in a pyrex pressure reactor at elevated temperature. Although some orange coloration occurred, consistent with the desired polymerization, TLC analysis of the cooled solution showed the presence only of unreacted aldehyde.

The self-condensation was attempted next with trifluoroacetic anhydride (TFAA). Similar reactions have been reported in the literature; for example, 2-methylpyridine was reacted with benzaldehyde in an acetic anhydride / acetic acid mixture to give the monopyridine analogue of stilbene[8]. Reaction of pyridine aldehyde in TFAA was attempted at various temperatures and for varying times to see if any reaction might occur. Again, however, TLC showed only unreacted starting material.

The polymerization was then attempted under basic conditions using lithium diisopropylamine (LDA)[9]; there is ample precedent for deprotonation of 2-methylpyridines. A solution of diisopropylamine in THF was cooled to -78 °C, and n-butyllithium added; after stirring for a short time, the aldehyde in THF was added, and the mixture slowly warmed to room temperature. After aqueous workup, the organic layer was checked by TLC; no starting material remained.

This reaction was attempted on a small scale, and the product was not isolated. The next stage in this project is to repeat the reaction on a larger scale, attempting to isolate, purify and characterize the product.

4.3 Further Research Possibilities

The target being pursued in this project is only a model compound; the terminal methyl and aldehyde groups are not ideal surface-linking groups. Ultimately, the goal is to prepare a polymer of 2-methyl-5-pyridine carboxaldehyde with terminating groups more useful for linking to a metal surface.

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8. See Ref. 3.
9. See Ref. 3.

Chapter 5: Polymeric Polyimine Synthesis

5.1 Introduction

The azo dye esters discussed in Chapter 3 and the polypyridine discussed in Chapter 4 are examples of fully conjugated, dipolar, rigid-rod molecules. In this chapter, the focus of the discussion is a different type of target.

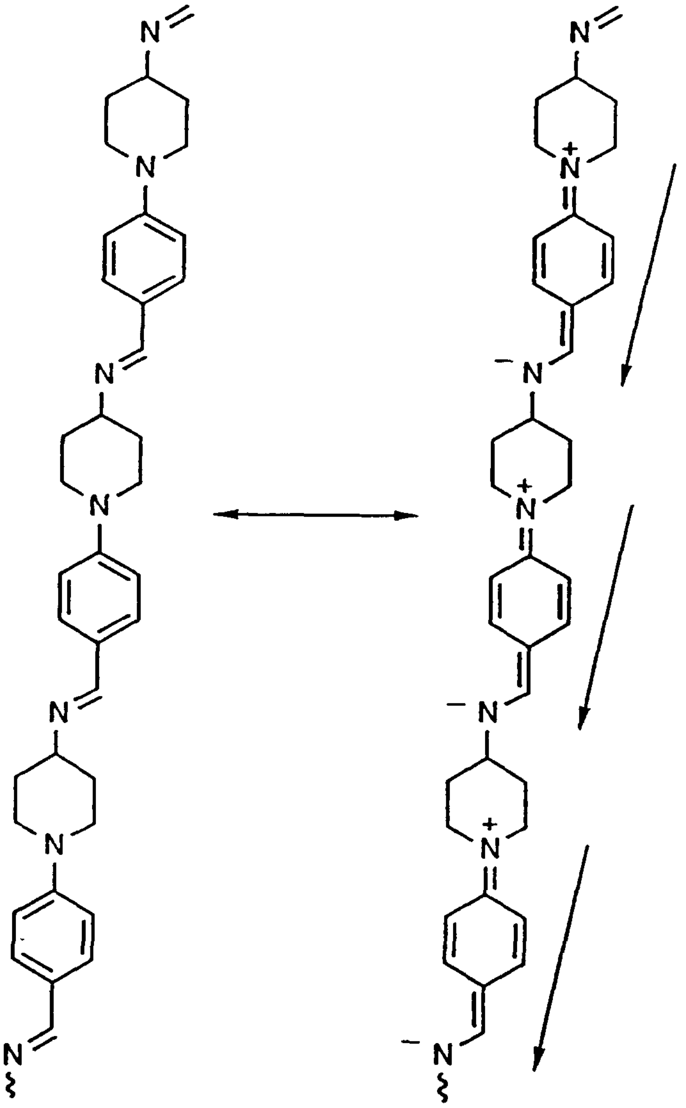
As shown schematically in Figure 5.1, dipolar rigid-rod molecules may be considered in two broad classes: fully conjugated molecules, and incompletely conjugated molecules. In both classes, the dipole moment of the polymer will be the vector sum of the individual monomer dipoles. In both classes, the rigidity and linearity of the polymer will be dependent on the individual monomers. Due to the differences in conjugation, however, the uv / visible absorption spectra for the two classes may be quite different.

Our goal in pursuing this second type of target is to prepare a series of molecules with a given chromophore (in order to control the position of maximum absorption) and a large dipole moment (in order to maximize dipolar alignment). What is needed is an insulating linking group that will separate the individual chromophores but allow the dipole moments to add maximally.

The 4-piperidinylimino acts as an ideal linker for the preparation of rigid-rod, dipolar molecules. This group maintains dipole additivity between the two respective chromophores[1]. By aligning the dipolar monomers in a linear,

Figure 5.1

Polymeric Dipolar Organic Rod based on Insulated, Aligned Fragments



head-to-tail fashion, the polymer (oligomer) dipole moment is approximately the sum of the individual monomer dipoles. Since the ability to be oriented by an electric field is proportional to the dipole moment of the molecule, these polymers (oligomers) should be efficiently aligned by an electric field.

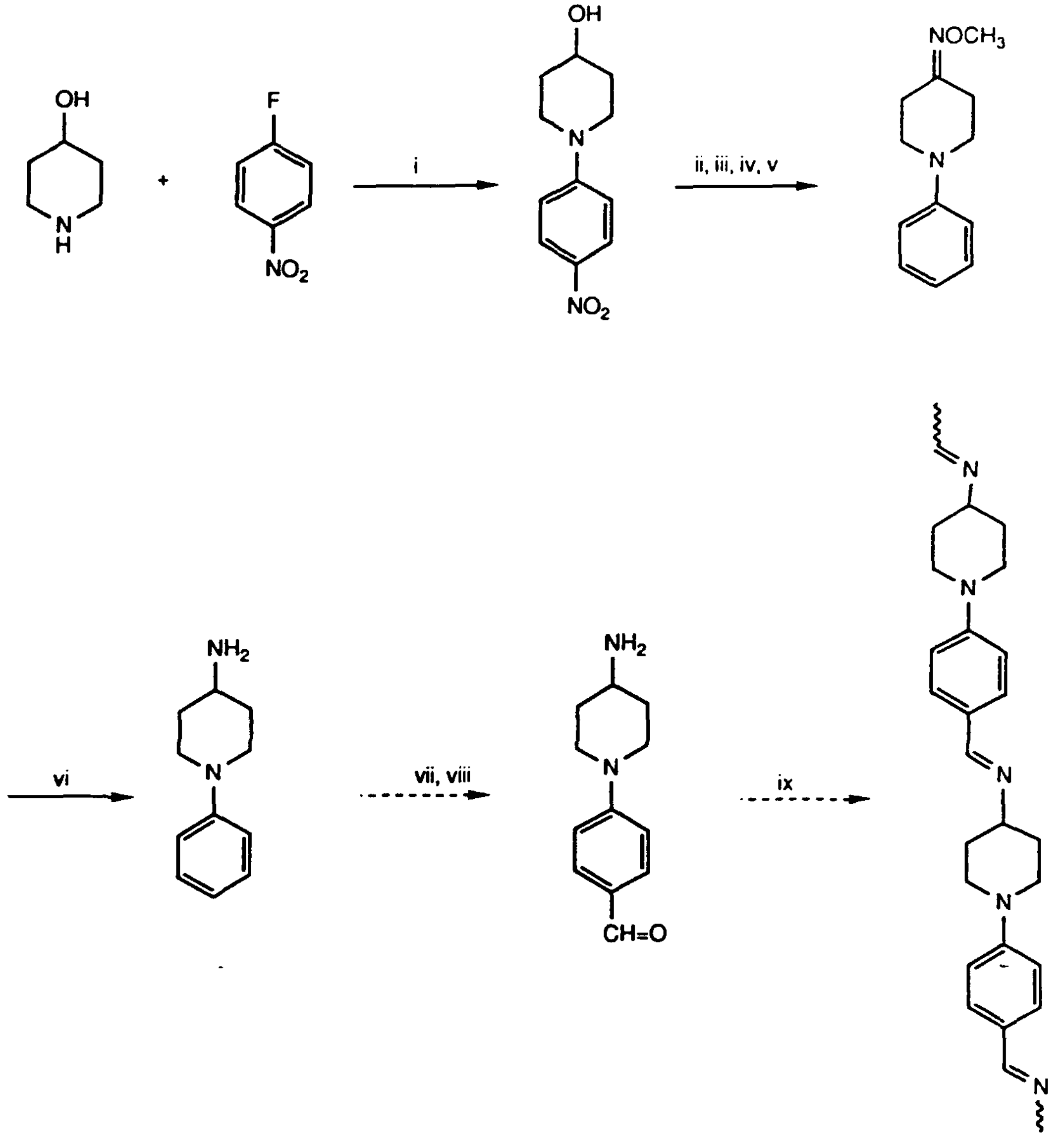
5.2 Synthesis

The reaction of 4-piperidinol with 4-fluoronitrobenzene, followed by transfer hydrogenation of the nitro group[2] (see Fig. 5.2 for synthesis scheme) yielded the aromatic diamine. Diazotization of the primary amine, followed by deamination with hypophosphorous acid[3], yielded the alcohol. Oxidation to the ketone was done via a Swern oxidation[4], and the ketone converted to the oxime ether using methoxylamine hydrochloride[5]. This two-step sequence for conversion of ketone to amine was chosen because previous investigation on related systems had shown that the ketone could not be converted into the amine directly by reductive amination[6]. The oxime ether was reduced[7] to the amine with BH_3 / THF.

This is the point to which the synthesis has been carried. From here, the proposed route to be investigated is trifluoro-acetylation of the primary amine, followed by Villsmeier formylation[8] and amide hydrolysis; this should yield the target monomer. The polyimine would be formed with self-polymerization of this monomer. Alternatively, the Villsmeier formylation may be replaced by azo coupling to the

Figure 5.2

Synthesis of Polyimine



i. acetonitrile, TEA, reflux; ii. cyclohexene, 10%Pd/C, EtOH, reflux; iii. $NaNO_2$, H_3PO_2, EtOH, water; iv. DMSO, oxalyl chloride, TEA, CH_2Cl_2 ; v. methoxylamine, pyridine / ethanol; vi. borane / THF; then, aqueous NaOH; vii. trifluoroacetic anydride; viii. phosphorous oxychloride, N,N-dimethylformamide; then, aqueous NaOH; ix. molecular sieves, toluene diazonium ion obtained from p-aminobenzaldehyde.

5.3 Results and Discussion

The difficulty in carrying out the later steps of the synthesis has been based on a large mass loss in the reaction converting the ketone to the oxime ether. The oxime ether recovered has been found to be relatively pure; once the yield problem is solved, the subsequent steps in the synthesis can be attempted.

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Chapter 6: Experimental Procedures

6.1 General Experimental Procedures

All reagents were utilized as obtained unless otherwise indicated. THF was distilled from sodium / benzophenone. DMSO and CH_2Cl_2 were distilled from CaH_2. Melting points were obtained in open capillaries in a Thomas Hoover apparatus and are uncorrected. Infrared spectra were obtained using a Perkin-Elmer 1320 Spectrophotometer. ^1H NMR spectra were obtained at room temperature using a General Electric QE300 instrument. Chemical shifts are reported in ppm downfield from tetramethylsilane. Gas chromatography / mass spectrometry data were determined on a Hewlett-Packard 5928 instrument, operating in the electron impact mode.

TLC was performed using Baker IB2-F silica or aluminum oxide IB-F plates (2.5 x 7.5 cm); the chromatograms were visualized by short-wave (254 nm) ultraviolet light. Column chromatography was performed on silica (Merck, Grade 60, 230-400 mesh) or alumina (activated, basic, Brockmann I, Standard Grade, 150 mesh) gel.

6.2 Azo Dye Project Experimental Procedures

Coupling of p-aminobenzoic acid and dioctadecylaniline via two different methods:

(1) Formation of a diazonium ion in a water/HCl Solution: Synthesis of 4-[[4-(diocatodecylamino)phenyl]azo]-benzoic acid: To a solution of p-aminobenzoic acid (559 mg, 4.08 mmol)

in 4:1 water/conc. HCl (5 ml) cooled to 0 °C, aqueous sodium nitrite (341.3 mg) in 1-1.5 ml H_2O, was added dropwise maintaining the temperature at 3-5 °C. To half the total volume of the diazonium solution, tetrafluoroboric acid (1 ml) was added and the solution cooled in an ice bath, yielding fine, white crystals. The diazonium salt crystals were collected and added to a solution of dioctadecylaniline (302 mg, 0.51 mmol) in glacial acetic acid (5 ml) at room temperature and stirred for 24 hours. The product was collected by gravity filtration, and dried under vacuum to yield a dark red solid (45 mg, 12.2%): mp 82 °C ^{1}H NMR ($CDCl_3$) 9.95 (s, 1H), 8.18 (d, 2H, J = 10 Hz), 7.89-7.83 (m, 4H), 6.69 (d, 2H, 11 Hz), 3.47 (t, 4H), 1.66-1.58 (m, 4H), 1.41-1.20 (m, 60H).

(2) 4-Benzenediazonium carboxylic acid tetrafluoroborate: A solution of fluoroboric acid (35 mL of 50% aqueous HBF_4) was cooled to approximately 0 °C, in an ice / salt / water bath, and 4-amino-benzoic acid (13.7 g, 0.1 mol) was added. The ice / salt / water bath was replaced with an ice water bath and a solution of sodium nitrite (6.9 g, 0.1 mol, in 10 ml water) was added dropwise to the solution below the level of the liquid, over 15 minutes. The solution was stirred for 15 minutes at 0 °C; the solid was collected in a fritted glass funnel, and air dried on a porcelain plate, yielding a white solid (13.7 g, 58.05 %): ^{1}H NMR (acetone-d_6) 8.88 (d, 2H, J = 6 Hz), 8.50 (d, 2H, J = 9 Hz), 6.01 (s, 1H); IR 2800-3000

(broad, s), 1720 (s), 1460 (m), 1380 (m), 1220-1330 (broad, s), 980-1160 (broad, s) cm^{-1}.

Coupling of 4-Benzenediazonium carboxylic acid tetrafluoro-borate with N,N-dioctadecylaniline: To a solution of dioctadecylaniline (1.69 g, 2.82 mmol) in glacial acetic acid (30 ml), the diazonium ion (665 mg, 2.82 mmol) was added, at room temperature, and stirred vigorously. Upon addition of the diazonium ion, a red solid began to precipitate. After approximately 12 hours, the solution was diluted with water (30 ml); the solid was collected by filtration, washed with a 1:1 water / acetic acid solution, and dried under vacuum, yielding red solid (1.866 g, 88.51 %): m.p. = 82 ° C; ^{1}H NMR ($CDCl_3$) 9.95 (s, 1H), 8.18 (d, 2H, J = 10 Hz), 7.89-7.83 (m, 4H), 6.69 (d, 2H, 11Hz), 3.47 (t, 4H), 1.66-1.58 (m, 4H), 1.41-1.20 (m, 60 H), 0.91 (t, 6H).

Esterification of azo acid with 1H1H,2H,2H-perfluorododecan-1-ol: A methylene chloride (0.4 mL) solution of the free acid (75.8 mg, 0.1 mmol), 1H,1H,2H,2H-perfluorododecan-1-ol (53.5 mg, 0.095 mmol), DCC (33 mg, 0.16 mmol), and DMAP (14 mg, 0.11 mmol), combined in that order, was stirred at room temperature for 24 hours. The solution was washed with 0.1 M HCl (2 x 10 ml). The organic layer was dried (sodium sulfate) and the solvent removed at reduced pressure. The product was purified by chromatography on silica gel, eluting with diethyl ether. The solvent was evaporated at reduced pressure and dried under vacuum to yield an orange-red wax (120 mg, 92.3%): ^{1}H NMR ($CDCl_3$) 8.13 (d, 2H, J = 8.5 Hz), 7.88 (d, 2H, J = 4 Hz), 7.852 (d, 2H, J = 3.5 Hz), 6.72-6.60 (m, 2H), 4.66 (t, 2H), 3.33-3.13 (m, 4H), 2.69-2.48 (m, 4H), 1.6-1.1 (m, 60H), 0.88 (t, 6H).

Small scale esterification of azo acid with poly(ethylene glycol), methyl ether To a solution of the azo acid (45 mg, 0.06 mmol) in methylene chloride (5 ml), DCC (approx. 35 mgs) was added. After stirring for 15 minutes, poly(ethylene glycol) methyl ether (25 mg, ≈0.07 mmol) was added and the solution was stirred at room temperature for 24 hours. The solvent was evaporated at reduced pressure and the product separated from the acid by silica gel chromatography eluting with diethyl ether followed by ethyl acetate. Fractions were analyzed by TLC; those containing product were combined, and the solvent was evaporated at reduced pressure, to give the product ester, contaminated with dicyclohexylurea: ^{1}H NMR ($CDCl_3$) 8.08 (d, 2H, J = 9 Hz), 7.82-7.75 (m, 4H), 6.68 (d, 2H), 3.88-3.32 (m, 4-19H), 1.97-1.90 (m, 4H), 1.75-1.55 (m, 4H), 1.42-0.96 (m, 60H), 0.80 (m, 6H).

Esterification of azo acid with poly(ethylene glycol) methyl ether A methylene chloride (0.5 mL) solution of the azo acid (238.2 mg, 0.319 mmol), poly(ethylene glycol) methyl ether (0.1 ml, 0.304 mmol), DCC (64.1 mg, 0.311 mmol, dissolved in a small amount of methylene chloride), and DMAP (36.6 mg, 0.299 mmol), combined in that order, was stirred at room temperature for 24 hours. The product was purified by chromatography on alumina gel, eluting with acetone. Fractions containing product were combined and the solvent was evaporated at reduced pressure to yield the yellow-red wax (336.3 mg, 96.2 %). ^{1}H NMR ($CDCl_3$) 8.15 (d, 2H, J = 10 Hz), 7.91-7.82 (m, 4H), 6.68 (d, 2H), 4.50 (t, 2H), 3.88-3.32 (m, 4H), 1.89 (m, 4H), 1.62 (m, 4H), 1.49-1.15 (m, 60H), 0.87 (t, 6H).

Attempted esterification of methyl red with TFAA A solution of poly(ethylene glycol) methyl ether (0.42 g, 1.2 mmol) and the sodium salt of methyl red (0.35 g, 1.2 mmol), in trifluoroacetic anhydride (1.51 g, 7.2 mmol) and toluene (4 ml) was stirred at room temperature for 24 hours. No product could be detected by TLC (silica gel, eluted with CH_2Cl_2).

Attempted synthesis of acid chloride from azo acid To a solution of the azo acid (183.7 mg, 0.246 mmol) in toluene (1.5 ml) at 40 °C, under nitrogen, triethylamine (24.9 mg, 0.246 mmol) was added, and the solution was heated for 15 minutes. Thionyl chloride (29.3 mg, 0.27 mmol) was added to the solution at 48 °C and the reaction was heated to reflux (60-70 °C) for two hours. TLC analysis (silica gel plate, 4:1 ethyl acetate-acetic acid eluent) showed acid only. A large excess of thionyl chloride (~0.5 ml) was added and the solution was stirred at 40 °C for three more hours. TLC showed a major zone at high R_f; no acid remained. The reaction mixture was chromatographed on silica gel eluting with ethyl acetate; the colored bands were collected and combined.

This route was abandoned after succesful esterification using the DCC/DMAP procedure was obtained.

6.3 Poly(imine) Experimental Procedures

N-(phenyl)-4-piperidinol To a solution of N-(4-aminophenyl)-4-piperidinol (18.5 g, 96.2 mmol) in ethanol (200 ml), hypophosphorous acid (300 ml of 50% aqueous solution) was added; the solution was cooled to 5 °C and stirred for 30 minutes. Aqueous sodium nitrite (8.28 g, 0.12 mol) in 4.5 ml water was slowly added, maintaining the temperature below 10 °C. After complete addition, the reaction was stirred at room temperature for 48 hours. The solution was made alkaline with 30% aqueous sodium hydroxide, and extracted with ethyl acetate (3 x 10 ml). The organic layer was dried (Na_2SO_4), and the solvent evaporated at reduced pressure to yield a tacky, black gum. The residue was purified by silica gel chromatography eluting with ethyl acetate; the high R_f product (silica gel, EtOAc elution, swuv) was collected and the solvent was evaporated at reduced pressure to yield a viscous, yellow oil (1.5 g, 8.79%): ^{1}H NMR ($CDCl_3$) 7.13 (m, 2H), 6.98 (m, 2H), 6.93 (m, 1H), 3.62-3.50 (m, 2H), 2.99-2.85 (m, 2H), 2.0-1.96 (m, 2H), 1.78-1.65 (m, 2H).

This reaction could be reproduced on a smaller scale with better yield.

N-(phenyl)-4-piperidone To a solution of oxalyl chloride (1.39 g, 0.011 mmol) in methylene chloride (25 ml), under nitrogen, at -76 °C, a solution of DMSO (1.87 g, 24 mmol, freshly distilled from calcium hydride) in methylene chloride (15 ml) was added, via an addition funnel, over an eight minute period. The mixture was stirred for 10 minutes. A solution of the N-(phenyl)-4-piperidinol (1.77 g, 10 mmol) in methylene chloride was similarly added over an eight minute period, maintaining the temperature below -60 °C. The mixture was stirred for 20 minutes. Triethylamine (6.66 ml, 4.83 g, 0.048 mol) was similarly added over a four minute period, and the mixture left on the dry ice / chloroform cooling bath for nine minutes. The solution was warmed to room temperature, stirred for 15 minutes, and quenched with water (30 ml). The aqueous layer was extracted with methylene chloride (2 x 10 ml), and the organic layer washed with 1M HCl (10 ml). After drying with Na_2SO_4, the product was isolated by silica gel chromatography eluting with ethyl acetate. The solvent was evaporated at reduced pressure, and then under high vacuum to yield the tacky, dark brown product (0.88 g, 50.1%): ^1H NMR ($CDCl_3$) 7.32 (t, 2H), 6.98 (d, 2H), 6.88 (t, 1H), 3.61 (t, 4H), 2.58 (t, 4H).

Formation of oxime ether To a solution of N-(phenyl)-4-piper-idone (0.8 g, 4.54 mmol) in ethanol (5 ml), triethylamine (0.634 ml, 0.46 g, 4.5 mmol), methoxylamine hydrochloride (0.6 g, 7.18 mmol), and 4Å molecular sieves were added and the solution was refluxed for two hours. The ethanol was evaporated at reduced pressure. The residue was dissolved in ethyl acetate and the solution was filtered to remove the molecular sieves. The solvent was evaporated at reduced pressure; the product was dried under vacuum to yield the oxime ether. (0.5 g, 53.7%): ^{1}H NMR ($CDCl_3$) 7.27 (t, 2H, J = 8.5 Hz), 6.93 (d, 2H, J = 8 Hz), 6.86 (t, 1H), 3.86 (s, 1H), 3.42 (t, 2H), 3.32 (t, 2H), 2.71 (t, 2H, J = 6.5 Hz), 2.48 (t, 2H, J = 6 Hz).

N-(phenyl)-4-aminopiperidine To a solution of the oxime ether (0.5 g, 2.4 mmol) in dry tetrahydrofuran (3 ml), under nitrogen, at 0 °C, borane-tetrahydrofuran (8 ml of 1.0 M solution, 8 mmol) was added in small portions, with the reaction temperature maintained below 5 °C. After stirring at room temperature for 24 hours, and quenching with 20% potassium hydroxide until evolution of H_2 had ceased, the organic layer was separated. The aqueous layer was extracted with diethyl ether (2 x 10 ml) and the combined organic solutions dried with Na_2SO_4; the solvent was evaporated at reduced pressure to yield a tacky, black tar (0.39 g, ~78%): ^{1}H NMR ($CDCl_3$) 7.18 (t, 2H), 6.87 (d, 2H), 6.76 (t, 1H), 3.56 (t, 2H), 3.49 (t, 2H), 2.88 (t, 2H), 2.69 (t, 2H).

6.4 Poly(pyridinevinylene) Experimental Procedures

Reduction of 6-methyl nicotinic acid To a solution of borane-tetrahydrofuran (48 ml of 1.0 M solution, 48 mmol) in THF (10 ml), under nitrogen, at 0 °C, 6-methylnicotinic acid (0.781 g, 5.7 mmol) in tetrahydrofuran (5 ml) was added over a period of five minutes. After addition, the reaction was stirred at room temperature for 24 hours. The solution was cooled to 0 °C, and 20% aqueous potassium hydroxide carefully added until evolution of H_2 ceased. The organic layer was separated; the white precipitate and the aqueous layer were washed with diethyl ether (3 x 7 ml), and combined with the organic layer. The organic layer was dried (Na_2SO_4); the solvent was evaporated at reduced pressure, and residual butanol removed under vacuum, yielding opaque, white, waxy solid (446 mg, 57.1%): ^1H NMR (DMSO-d_6) 8.53 (s, 1H), 7.88 (d, 1H, J = 10.5 Hz), 7.52 (d, 1H, 10.5 Hz), 4.5 (d, 2H), 2.53 (s, 3H).

Attempted Swern Oxidation of Alcohol To a solution of oxalyl chloride (1.42 g, 11.2 mmol) in methylene chloride (20 ml), under nitrogen, at -60 °C, dimethyl sulfoxide (1.8 g, 23 mmol) was added over five minutes; all reagents were added via addition funnels, flushed with nitrogen. The solution was stirred for five minutes and the alcohol (1.25 g, 10.16 mmol) in methylene chloride (5 ml) was added over five minutes. The solution, still at -60 °C, was stirred for 30 additional minutes. Triethylamine (6.41 ml, 4.65 g, 45.9 mmol) was added over five minutes; the reaction was stirred for 10 minutes, removed from the cooling bath, and stirred at room temperature for two hours. Water (31 ml) was added, and the organic layer was separated. The aqueous layer was re-extracted with methylene chloride, and the organic solutions combined. No product was detected by TLC (silica gel plate, eluted with ethyl acetate, swuv light) in the organic layer. The aqueous layer showed no product when checked by gas chromatograph.

PCC Oxidation of alcohol to aldehyde To a solution of the 2-methyl-5-hydroxymethylpyridine (590 mg, 4.79 mmol) in methylene chloride (10 ml), pyridinium chlorochromate (1.5 g, 6.96 mmol) was added. The solution was stirred at room temperature for 48 hours. The organic solution was decanted from the gummy residue; the residue was washed with diethyl ether (4 x 15 ml) until a black, powdery solid remained, and the washings were combined with the original organic phase. The organic solution was filtered through a short silica gel column eluting with diethyl ether. The solvent was evaporated at reduced pressure to yield a yellow-green oil that partially crystallized upon standing (240 mg, 41.4%): ^{1}H NMR (DMSO) 10.0 (s, 1H), 8.89 (s, 1H), 8.01 (d, 1H, J = 13.5 Hz), 7.27 (d, 1H, J = 14 Hz), 2.60 (s, 3H).

Attempted polymerization of aldehyde using TFAA A solution of 2-methyl-5-pyridinecarboxaldehyde (42.2 mg, 0.35 mmol) in trifluoroacetic anhydride (2.08 g, 0.01 mmol) in a high pressure reaction chamber was heated to 80-90 °C for 45 minutes and cooled to room temperature. The TFAA was evaporated at reduced pressure and NMR revealed almost entirely starting aldehyde; a small amount of product may have formed.

The reaction was repeated on a same scale, except the reactants were heated to a maximum temperature of 116 °C, with a total heating time of 80 minutes. The solution was tested by TLC (silica gel plate, ethyl acetate eluent). Two zones were seen, both of which absorbed light in the ultraviolet region and neither of which corresponded to the starting aldehyde.

The reaction was repeated again, this time heating for seven hours at between 112-130 °C. However, only aldehyde was observed by TLC.

Although the first two trials seem to have indicated the reaction might yield product, this method was abandoned due to difficulty in obtaining product reproducibly.

Attempted polymerization of aldehyde with zinc chloride To zinc chloride (13 mg, 0.095 mmol), at 85 °C, under argon, aldehyde (30 mg, 0.25 mmol) was added. The solution was heated at 120-140 °C for 20 hours, and then allowed to cool to room temperature. The reaction was partitioned between water (0.5 ml) and methylene chloride (0.5 ml). The methylene chloride was dried and the red solution checked by TLC (silica gel plate, ethyl acetate eluent). Three minor zones were observed; however, aldehyde was the major constituent.

Polymerization with LDA To a solution of diisopropylamine (0.058 ml, 41.8 mg, 0.413 mmol) in distilled THF, at -78 °C, under nitrogen, n-butyllithium (0.200 ml, 0.411 mmol) was added via syringe. The aldehyde (48.5 mg, 0.40 mmol) was added via syringe; the mixture was stirred for 20 minutes and then allowed to warm to room temperature. A solution of saturated NH_4Cl (5 ml) was diluted with an equal amount of distilled water and the solution added to the reaction mixture. The aqueous phase was extracted with organic solvents (CH_2Cl_2, EtOAc, $CHCl_3$, and Et_2O), dried (Na_2SO_4), and the solvents were evaporated at reduced pressure. TLC analysis (silica gel, eluted with EtOAc) revealed no evidence of aldehyde, only one primary higher R_f zone. The treatment of this product with TFAA to establish if dehydration will yield the vinylene polymer is underway.

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